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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>5</sup> : A01N 37/16 // (A01N 37/16, 25:30)</p>	<p>A1</p>	<p>(11) International Publication Number: WO 94/14321 (43) International Publication Date: 7 July 1994 (07.07.94)</p>
<p>(21) International Application Number: PCT/GB93/02520 (22) International Filing Date: 9 December 1993 (09.12.93) (30) Priority Data: 9227020.6 24 December 1992 (24.12.92) GB (71) Applicant (for all designated States except US): SOLVAY INTEROX LIMITED [GB/GB]; Baronet Works, Baronet Road, Warrington, Cheshire WA4 6HB (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): FRENCH, Madeline, Susan [GB/GB]; 12 Delphfield, Norton Cross, Runcorn WA7 6RW (GB). HARVEY, Anita, Jane [GB/GB]; 87 Dove Close, Birchwood, Warrington WA3 6QH (GB). (74) Agent: PEARCE, Timothy; Solvay Interlox Limited, Patent Department, P.O. Box 51, Moorfield Road, Widnes WA8 0FE (GB).</p>	<p>(81) Designated States: AU, BB, BG, BR, BY, CA, CZ, FI, HU, JP, KP, KR, KZ, LK, LV, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.</p>	
<p>(54) Title: MICROBICIDAL COMPOSITIONS</p> <p>(57) Abstract</p> <p>Microbicidal compositions having activity over a broad pH range are provided. The compositions comprise a peracid and a nonionic surfactant according to the general chemical formula: <math>R-(OCH_2CH_2)_n-(OCH_2CH_2CH_3)_p-O-R'</math>, wherein R represents an alkyl group of at least 6 carbon atoms, n and p each represent an integer, and R' represents a short alkyl group of less than 6 carbon atoms. The compositions can additionally comprise a cationic surfactant.</p>		

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### Microbicidal Compositions

The present invention concerns microbicidal compositions. More specifically, the present invention concerns peracid microbicidal compositions, and still more specifically, peracid microbicidal peracid compositions having  
15 activity over a broad pH range.

The use of aliphatic peracids as microbicides is well known in the art. Such solutions have found favour because they offer a microbicidal system which has reduced environmental impact and are completely biodegradable. It has also long been recognised that the microbicidal activity of aliphatic peracids is  
20 strongly dependant on the pH at which the peracid is employed, and that the activity decreases as the pH increases. This is particularly evident as the pH of the peracid solution approaches neutral pH. Accordingly, the most effective use of aliphatic peracid microbicides has hitherto occurred at acidic pH. A number of systems require disinfection at alkaline pH or exist in their natural  
25 state at alkaline pH, and are thus not well suited to disinfection by such peracid-based microbicides. It remains an ongoing desideratum to identify peracid-based microbicide compositions having activity over a broader and/or higher pH range.

It is an object of certain aspects of the present invention to provide  
30 aliphatic peracid microbicide compositions having improved activity over a broader and/or higher pH range.

It is a further object of some or other aspects of the present invention to provide microbicidal compositions having improved activity against gram-negative bacteria over a broader and/or higher pH range.

35 According to the present invention, there are provided peracid compositions having microbicidal activity over a broad pH range, characterised in that they

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comprise an effective amount of a peracid and a nonionic surfactant according to the general chemical formula (1):



wherein R represents an alkyl group of at least 6 carbon atoms n and p each  
5 represent an integer, and R' represents a short alkyl group of less than 6  
carbon atoms.

According to a second aspect of the present invention, there is provided a  
microbicidal process employing as microbicide an effective amount of a peracid  
and a nonionic surfactant, characterised in that the nonionic surfactant has the  
10 general formula:  $R-(OCH_2CH_2)_n-(OCH_2CH_2CH_3)_p-O-R'$   
wherein R represents an alkyl group of at least 6 carbon atoms n and p each  
represent an integer, and R' represents a short alkyl group of less than 6  
carbon atoms.

By employing the selected alkoxyated alcohol surfactant of formula (1), it  
15 has been found that the effectiveness of peracid microbicides is enhanced at  
treatment pHs of above pH 6, i.e. in approximately neutral or mildly alkaline pH  
conditions, thereby extending advantageously the effective treatment range for  
the peracids.

In formula (1), R often contains from about 6 to about 18 carbons, and  
20 especially from about 8 to about 12 carbons and in many instances comprises  
a linear group. R can be synthetically derived, or can be obtained from natural  
sources, for example, from tallow. R' in formula (1) often contains from 2 to 4  
carbon atoms and typically comprises 3 carbon atoms. The weight proportion  
of alkoxyate i.e. ethoxyate or the total of ethoxyate and propoxyate in the  
25 surfactant is often selected in the region of about 55% to about 90%; n + p in  
formula (1) in many instances totalling from 4 to 20.

It will be recognised that compositions according to the present invention  
can be supplied in a number of different forms or can be produced immediately  
prior to use depending, for example, on the particular composition desired, or  
30 on the particular application. For instance, in certain embodiments of the  
present invention, the composition is in the form of a ready-to-use solution  
which can be used without requiring dilution. In certain other embodiments,  
the composition is in the form of a concentrated solution which may be  
employed without dilution, but is primarily intended for dilution prior to use. In  
35 further embodiments, the components are provided as a two pack system, with  
the first solution comprising aqueous peracid solution and optionally a fraction  
of the nonionic surfactant, and the second solution comprising the remaining

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fraction of the nonionic surfactant. In these two pack systems, the second solution can be used to dilute the first solution to produce a composition ready for immediate use, or a composition which can be diluted further prior to use.

The weight of alkoxyated alcohol in the invention compositions can be selected within a wide range. In many embodiments, where the compositions are ready for use or supplied as a concentrate, it is at least 0.1% w/w and often is not greater than about 50% w/w. Advantageous results have been obtained for ready to use solutions at a concentration chosen in the range of about 4 to about 15% w/w of the alkoxyated alcohol. Where a concentrate is diluted prior to use, the concentration of alcohol ethoxylate in the in use solution is often in the range of from about 0.1% w/w to about 15%w/w.

Where the components are provided as a two pack system, the second solution can contain up to 100% of nonionic surfactant, however, in many embodiments, the nonionic surfactant will be present at from about 20% w/w to about 80% w/w. When nonionic surfactant is employed in the first solution in a two pack system, the concentration of the nonionic surfactant is typically in the range of from about 4 to about 25% w/w.

The peracid can comprise any percarboxylic acid, particularly water-soluble percarboxylic acids and especially is selected from low or medium molecular weight aliphatic percarboxylic acids such as those containing up to 9 carbons. The invention will be described with particular reference to peracetic acid, but for example, perpropionic acid may be employed instead of or together with peracetic acid.

The concentration of peracid in preformed compositions intended for storage and/or transportation can be selected over a wide range, such as from about 0.01% to 40% w/w. In many embodiments, the compositions comprise a dilute solution of the peracid, such as from about 0.5% to about 10% w/w. The actual selection of the peracid is often a matter at the discretion of the producer, for his own convenience, balancing the beneficial and disadvantageous effects of a chosen concentration. Concentrations of around 2 to 3% w/w peracid and from about 4 to about 5.5% w/w peracid are quite popular as compromises that are readily transportable without transporting too much water.

In many desirable compositions according to the present invention, which are intended for storage and or transportation, the peracid is made by a reaction between the corresponding carboxylic acid or carboxylic acid anhydride and hydrogen peroxide in an aqueous medium. It is particularly

desirable to employ compositions in which the peracid is present at a concentration that is substantially in equilibrium with residual concentrations of its corresponding carboxylic acid and hydrogen peroxide. In such compositions, the concentration of hydrogen peroxide is often selected in the  
5 range of from about 0.1 to 30% w/w and the concentration of carboxylic acid from about 0.5 to about 50% w/w. In practice, the weight ratio of carboxylic acid e.g. acetic acid or hydrogen peroxide relative to the peracid can be varied at the discretion of the producer/user within the entire range, provided that an appropriate concentration of the other reagent is present. In general terms, for  
10 a stable equilibrium, a low peroxide concentration is balanced by a high carboxylic acid concentration, and vice versa, and ratio of peroxide plus carboxylic acid to peracid increases as the concentration of peracid decreases. For many dilute, transportable peracid compositions containing less than 6% peracid, the weight ratio of peroxide to peracid and of carboxylic acid to  
15 peracid are each often selected in the range of from about 1:10 to about 10:1.

The transportable compositions can be employed neat, for example in the disinfection of hard surfaces such as work surfaces, equipment or sanitary ware, particularly if they contain less than 6% peracid, but they are often diluted with water before use or it is an aqueous medium which it is intended  
20 to disinfect. The extent of dilution is at the discretion of the user, taking into account the extent and nature of the infecting micro-organisms which it is desired to kill, the period available for the kill and the operational conditions such as the temperature. Where the disinfection process involves a manual treatment stage, for example, distributing a composition over a hard surface  
25 with a cloth, it is often desirable that the peracid concentration in the solution in use is less than about 0.1%.

It is convenient to express the concentration of the disinfectant composition by reference to the concentration of the peracid. The alkoxylated alcohol is present at a relative concentration thereto as indicated previously  
30 herein. The peracid concentration is usually at least 5 mg/l and often up to 1000 mg/l. For a number of micro-organisms, a concentration of between 25 and 400 mg/l is selected. Depending on the conditions, though, for shock treatments, peracid concentration of above 1000 mg/l, for example up to about 10000 mg/l can be contemplated and for prolonged contact, a concentration of  
35 1 to 5 mg/l peracid can sometimes be appropriate.

It will be recognised that the advantage of the invention composition, compared with prior disclosed compositions not containing the alkoxylated

alcohol, is that it is relatively more effective at approximately neutral or mildly alkaline compositions, and especially at a pH of from above 6 to 8. The user can obtain the benefit of a similar extent of disinfection using a peracid composition, such as peracetic acid at a higher pH, i.e. avoiding or reducing the extent of pH adjustment, or alternatively he can obtain improved disinfection if he chooses not to acidify.

In theory, microbicidal compositions can contain other active microbicides in order to augment the activity from peracids, but there can be no guarantee that the addition of further components will improve the overall microbicidal effectiveness. Some combinations of peracid with other components are unstable and others show little or no detectable change in performance, at least with reference to various widespread target micro-organisms.

One such class of other microbicides comprises quaternary ammonium compounds, a class of cationic surfactants. They are widely available, and hence are attractive, but there can be difficulties associated with their use. Within the spectrum of micro-organisms that it is desired to control, i.e. kill or inactivate, by the application of a microbicidal composition are bacteria. Bacteria themselves are generally divided into two classes, gram-negative and gram-positive bacteria. It is generally recognised that, of the two classes, gram-positive bacteria are, in many cases, relatively easy to control by the application of quaternary ammonium compounds, but that gram negative bacteria are much more resistant to them. It is particularly desirable to control gram negative bacteria, because the group comprises many well known pathogens, for example, many species of faecal bacteria, pseudomonads which can cause skin irritation, and other species of bacteria, such as salmonella which can cause food poisoning. Self-evidently, it would be advantageous to identify microbicidal compositions having improved activity against gram negative bacteria.

It has been found to be especially desirable to employ the combination of peracid and alkoxylated alcohol in conjunction with a quaternary ammonium cationic surfactant, since by so doing, the resultant three component combination has been shown to be particularly effective against Gram negative bacteria. The quaternary ammonium compound, which can be represented by the general formula  $R^aR^bR^cR^dN^+ Q^-$  in which substituents  $R^a$ ,  $R^b$ ,  $R^c$ , and  $R^d$  each represent an alkyl or aryl group or two of which combine with the nitrogen to form a heterocyclic nucleus, the total number of carbons in  $R^a$  to  $R^d$  normally comprising from about 10 to about 30 carbons. One or two of



the substituents normally contains from 8 to 18 linear carbons often from C12 to C16, or forms part of the heterocyclic nucleus such pyridinium. One of the substituents can conveniently comprise a benzyl group. The remaining substituents usually are selected from C1 to C4 alkyl groups, and especially methyl or ethyl. Q represents a counterion such as hydroxyl, sulphate or alkyl sulphate.

The quaternary ammonium cationic surfactant (QACS) is often incorporated at a relatively small proportion of the overall composition, such as up to about 5% w/w in a dilutable composition, or up to about 0.5% w/w in a composition ready for use without further dilution. It will be recognised that in a two pack system, the QACS can be incorporated in either or both of the solutions at a concentration selected accordingly.

A particularly effective range of compositions comprises peracetic acid at a weight concentration in the region of about 2.0 to 5.5%, preferably in the presence of sufficient hydrogen peroxide and acetic acid selected together in the ranges of 1 to 20% and 1 to 50% respectively to obtain an equilibrium composition, from 4 to 15% alkoxylated alcohol and from 0.05 to 0.5% QACS. Such compositions may often be diluted by a factor in the range of from about 10 to about 1000, depending on the peracid concentration before dilution and its desired concentration for disinfection.

The invention compositions are particularly intended for use in the food, beverage and allied industries. The beverage industries include brewing, wine-making and alcohol distillation, and in dairies. In such industries, it is especially important to guard against the contamination of food and drink intended not only for human consumption, but also that intended for consumption by livestock, and pets. In such industries, the compositions can be used to disinfect brewing vessels, or surfaces that come into contact with prepared food or drink which in normal circumstances would be consumed without cooking. Those surfaces can include food mixing or washing vessels, transport equipment such as conveyors, and filling and packaging equipment. Compositions for use in these industries generally contain or are diluted in uses to peracid concentrations of below 500 mg/l with corresponding concentrations of the other constituents. Such diluted compositions in practice are rarely non-equilibrium in that over a period of time there would be a tendency for the peracid to re-equilibrate to hydrogen peroxide and carboxylic acid, but that is acceptable under disinfection treatment times. The use of the two component composition enables the process to be effected often without any pH alteration.

and the use of the three component composition is especially desirable in that it combines the advantage of the two component combination with that of a wider spectrum activity, even at approximately neutral or alkaline pH.

Having described the invention in general terms, specific embodiments thereof will be described hereinafter in greater detail by way of non-limiting example only.

Comparisons CA to CD and Examples 1 and 2

In Comparison CA, the treatment employed was a dilutable grade of peracetic acid commercially available from Solvay Interlox Limited under the Trade Mark PROXITANE, containing 5% peracetic acid, 10% w/w acetic acid and 20% w/w hydrogen peroxide, diluted to give an in use concentration of peracid of 50 mg/l for the bacteria, and 200 mg/l for the yeast.

In Comparison CB, the treatment employed comprised 0.2% w/v active ingredient of a quaternary ammonium cationic surfactant (QACS) available from Albright and Wilson under their Trade Mark EMPIGEN grade CM.

In Comparison CC, the composition employed comprised a solution of 10% w/v of an ethoxylated/propoxylated linear primary alcohol (alkoxylated alcohol) available from Union Carbide under their Trade Mark TRITON grade DF16.

In Comparison CD, the treatment employed was as in Comparison CA, except that 0.2% w/v active ingredient of the QACS of Comparison CB was also employed.

In Example 1, the treatment employed was as for Comparison CA, except that 10% w/v of the (alkoxylated alcohol) of Comparison CC was also employed.

In Example 2, the treatment employed was as for Example 1, except that 0.2% w/v active ingredient of the QACS of Comparison CB was also employed.

The effectiveness of each of the various Comparison and Example compositions as a microbicide was determined against three microbes considered to be representative for beverage industries, namely a yeast, Candida albicans, a gram negative bacterium, Pseudomonas aeruginosa, and a Gram-positive bacterium, Staphylococcus aureus.

The effectiveness of the composition as a microbicide was tested in a disinfectant suspension test. The microbicide was challenged with an inoculum of the microbe containing a measured concentration of between  $1 \times 10^8$  to  $3 \times 10^8$  cfu for bacteria and between  $1 \times 10^7$  and  $3 \times 10^7$  cfu for the yeast in the presence of yeast extract (0.4%) and standard hard water for a period of 5

minutes at ambient temperature. The composition was quenched in the standard manners for peracid and surfactants depending on which components are present and thereafter determining the number of viable micro-organisms by conventional plate culture techniques. The studies were conducted in  
5 duplicate.

The number of surviving viable bacteria or yeasts per unit volume (cfu) was then compared with the number before the disinfection treatment began, and the result given is the fraction that had been killed, expressed a logarithm, base 10; the higher the resultant number, the more effective the disinfection.  
10 The maximum for the yeast was 4.6, for the gram -ve bacterium was 6.3 and 5.9 for the Gram +ve bacterium.

The results of the disinfection studies are summarised in Table 1 below

Table 1

Trial		pH	Measured Log Reduction Factor for		
			Yeast	Gram -ve Bacteria	Gram +ve Bacteria
5	CA	4	4.5	6.3	5.9
		6	3.3	3.5	4.4
		8	1.8	2.3	1.7
		10	0.3	1.4	0.6
10	CB	4	0.4	3.8	5.9
		6	0.7	0	5.9
		8	3.4	0	5.9
		10	4.6	0	5.9
15	CC	4	0.5	1.9	1.8
		6	0.7	0	0.7
		8	0.6	0	0.9
		10	0.6	0	1.1
20	CD	4	4.6	6.3	5.9
		6	4.6	3.5	5.9
		8	4.6	2.3	5.9
		10	4.6	1.1	5.9
25	Ex 1	4	4.6	6.3	5.9
		6	4.1	6.3	5.9
		8	2.9	4.9	5.0
		10	0.6	1.9	1.9
30	Ex 2	4	3.1	6.3	5.9
		6	0.6	6.3	5.9
		8	4.6	6.3	5.9
		10	4.5	2.5	4.5

From Table 1, it can be seen in Comparison CA that the effectiveness of peracetic acid as a microbicide is very good at acidic pHs of the region of pH 4, but that its effectiveness diminishes as the pH of the solution containing the yeast or bacterium increases. A comparison of Comparisons CA with CB and CD shows that the QACS complements the peracetic acid in terms as the pH varies through the range tested for the yeast, without demonstrating synergism, but that there is no complementary action for the bacteria.

- A comparison of Comparisons CA, CC and Example 1 demonstrates that the combination of the alkoxylated alcohol and peracetic acid offers similar performance to that of peracetic acid alone, at the low pH, and at higher pHs of from pH6 to pH10 shows synergism especially for the Gram negative
- 5 bacteria which are resistant to QACS. Thus, Table 1 shows that the pH range in which peracids retain their effectiveness is visibly extended from about pH4 without the alkoxylated alcohol up as high as about pH8 with the alkoxylated alcohol. Table 1 also shows complementary results or synergistic results for the Gram positive bacteria and the yeast at the higher pHs.
- 10 From a comparison of Examples 1 and 2, it can be seen that the addition of the QACS is beneficial at the high end of the pH range, and particularly at about pH8, complementing the other components and producing a composition that is especially effective for all three of the test micro-organisms.
- 15 Storage Stability Trial
- To 247.5g of a sample of peracetic acid commercially available from Solvay Interlox Limited under the Trade Mark PROXITANE, containing 5% peracetic acid, 10% w/w acetic acid and 20% w/w hydrogen peroxide was added 0.11g of a quaternary ammonium cationic surfactant (QACS) available from Albright
- 20 and Wilson under their Trade Mark EMPIGEN grade CM and 2.39g of an ethoxylated/propoxylated linear primary alcohol (alkoxylated alcohol) available from Union Carbide under their Trade Mark TRITON grade DF16. After 160 days storage at ambient temperature (ca. 20 - 25°C), analysis of the sample showed that 95% of the peracetic acid was retained, indicating that the sample
- 25 had excellent storage stability.

## Claims:-

1. Peracid compositions having microbicidal activity over a broad pH range, characterised in that they comprise an effective amount of a peracid and a nonionic surfactant according to the general chemical formula (1):  
$$R-(OCH_2CH_2)_n-(OCH_2CH_2CH_3)_p-O-R'$$
wherein R represents an alkyl group of at least 6 carbon atoms n and p each represent an integer, and R' represents a short alkyl group of less than 6 carbon atoms.
2. A process for disinfection which comprises employing in combination a peracid and a nonionic surfactant according to the general chemical formula (1):  
$$R-(OCH_2CH_2)_n-(OCH_2CH_2CH_3)_p-O-R'$$
wherein R represents an alkyl group of at least 6 carbon atoms n and p each represent an integer, and R' represents a short alkyl group of less than 6 carbon atoms.
3. A composition or process according to claim 1 or 2 characterised in that the nonionic surfactant and peracid are present in a weight ratio selected within the range of from 10: 1 to 1 : 5, and preferably from 4 : 1 to 1 : 1.
4. A composition according to either preceding claim characterised in that the composition contains from about 1 to about 6% w/w peracid.
5. A composition according to any preceding claim characterised in that the peracid is peracetic acid.
6. A composition according to any preceding claim characterised in that it contains up to 0.5% w/w of a quaternary ammonium cationic surfactant.
7. A process for disinfection employing a composition as described in any preceding claim, either without or without dilution.
8. A process according to any of claims 2 to 7 characterised in that it is carried out at a pH of at least 6 and preferably from pH 6 to 8.

9. A process for preparing a composition according to any one of claims 1 or claims 3 to 6, characterised in that it comprises mixing a first solution comprising a peracid, with a second solution comprising a nonionic surfactant according to the general chemical formula (1):



wherein R represents an alkyl group of at least 6 carbon atoms n and p each represent an integer, and R' represents a short alkyl group of less than 6 carbon atoms.

10. A process or composition substantially as described herein with respect to any novel feature or novel combination of features.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 93/02520

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 A01N37/16 //(A01N37/16,25:30)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US,A,4 240 921 (T.J.KANIECKI) 23 December 1980 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

7 March 1994

Date of mailing of the international search report

16.03.94

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# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/GB 93/02520

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Quat + peracid



US005545374A

**United States Patent** [19]  
**French et al.**

[11] **Patent Number:** **5,545,374**  
[45] **Date of Patent:** **Aug. 13, 1996**

[54] **MICROBICIDAL COMPOSITIONS**  
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[21] **Appl. No.:** 464,743  
[22] **PCT Filed:** Dec. 9, 1993  
[86] **PCT No.:** PCT/GB93/02520  
§ 371 Date: Jun. 21, 1995  
§ 102(e) Date: Jun. 21, 1995  
[87] **PCT Pub. No.:** WO94/14321  
PCT Pub. Date: Jul. 7, 1994  
[30] **Foreign Application Priority Data**  
Dec. 24, 1992 [GB] United Kingdom ..... 9227020  
[51] **Int. Cl.<sup>6</sup>** ..... A61L 2/18; A01N 37/16  
[52] **U.S. Cl.** ..... 422/28; 510/218; 510/234; 510/372; 514/557; 252/186.42

[58] **Field of Search** ..... 422/28; 252/94, 252/95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 106

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[57] **ABSTRACT**  
Microbicidal compositions having activity over a broad pH range are provided. The compositions include a peracid and a nonionic surfactant according to the general chemical formula: R-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-(OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>p</sub>-OH, wherein R represents an alkyl group of at least 6 carbon atoms, and n and p each represent an integer. The compositions can additionally include a cationic surfactant.

**17 Claims, No Drawings**

includes Quat + peracid  
nonhalide

## MICROBICIDAL COMPOSITIONS

## BACKGROUND OF THE INVENTION

The present invention concerns microbicide compositions. More specifically, the present invention concerns peracid microbicide compositions, and still more specifically, peracid microbicide compositions having activity over a broad pH range.

The use of aliphatic peracids as microbicides is well known in the art. Such solutions have found favor because they offer a microbicide system which has reduced environmental impact and are completely biodegradable. For example, European patent application 0 193 41 6 discloses peracetic acid compositions comprising simple, non-capped alcohol ethoxylates. It has also long been recognized that the microbicide activity of aliphatic peracids is strongly dependent on the pH at which the peracid is employed, and that the activity decreases as the pH increases. This is particularly evident as the pH of the peracid solution approaches neutral pH. Accordingly, the most effective use of aliphatic peracid microbicides has hitherto occurred at acidic pH. A number of systems require disinfection at alkaline pH or exist in their natural state at alkaline pH, and are thus not well suited to disinfection by such peracid-based microbicides. It remains an ongoing desideratum to identify peracid-based microbicide compositions having activity over a broader and/or higher pH range.

It is an object of certain aspects of the present invention to provide aliphatic peracid microbicide compositions having improved activity over a broader and/or higher pH range.

It is a further object of some or other aspects of the present invention to provide microbicide compositions having improved activity against gram negative bacteria over a broader and/or higher pH range.

## BRIEF SUMMARY OF THE INVENTION

According to the present invention, there are provided peracid compositions having microbicide activity over a broad pH range, characterized in that they comprise an effective amount of a peracid and an ethoxylated and propoxylated alcohol nonionic surfactant according to the general chemical formula (1):



wherein R represents an alkyl group of at least 6 carbon atoms n and p each represent an integer.

According to a second aspect of the present invention, there is provided a microbicide process employing as microbicide an effective amount of a peracid and an ethoxylated and propoxylated alcohol nonionic surfactant, characterized in that the nonionic surfactant has the general formula:



wherein R represents an alkyl group of at least 6 carbon atoms n and p each represent an integer.

## DESCRIPTION OF PREFERRED EMBODIMENTS

By employing the selected nonionic alkoxylated alcohol surfactant of formula (1), it has been found that the effectiveness of peracid microbicides is enhanced at treatment

pHs of above pH 6, i.e. in approximately neutral or mildly alkaline pH conditions, thereby extending advantageously the effective treatment range for the peracids.

In formula (1), R often contains from about 6 to about 18 carbons, and especially from about 8 to about 12 carbons and in many instances comprises a linear group. R can be synthetically derived, or can be obtained from natural sources, for example, from tallow. The weight proportion of alkoxylate i.e. ethoxylate or the total of ethoxylate and propoxylate in the surfactant is often selected in the region of about 55% to about 90%; n+p in formula (1) in many instances totalling from 4 to 20.

It will be recognized that compositions according to the present invention can be supplied in a number of different forms or can be produced immediately prior to use depending, for example, on the particular composition desired, or on the particular application. For instance, in certain embodiments of the present invention, the composition is in the form of a ready-to-use solution which can be used without requiring dilution. In certain other embodiments, the composition is in the form of a concentrated solution which may be employed without dilution, but is primarily intended for dilution prior to use. In further embodiments, the components are provided as a two pack system, with the first solution comprising aqueous peracid solution and optionally a fraction of the nonionic surfactant, and the second solution comprising the remaining fraction of the nonionic surfactant. In these two pack systems, the second solution can be used to dilute the first solution to produce a composition ready for immediate use, or a composition which can be diluted further prior to use.

The weight of alkoxylated alcohol in the invention compositions can be selected within a wide range. In many embodiments, where the compositions are ready for use or supplied as a concentrate, it is at least 0.1% w/w and often is not greater than about 50% w/w. Advantageous results have been obtained for ready to use solutions at a concentration chosen in the range of about 4 to about 15% w/w of the alkoxylated alcohol. Where a concentrate is diluted prior to use, the concentration of alcohol ethoxylate in the diluted solution is often in the range of from about 0.1% w/w to about 15% w/w.

Where the components are provided as a two pack system, the second solution can contain up to 100% of nonionic surfactant, however, in many embodiments, the nonionic surfactant will be present at from about 20% w/w to about 80% w/w. When nonionic surfactant is employed in the first solution in a two pack system, the concentration of the nonionic surfactant is typically in the range of from about 4 to about 25% w/w.

The peracid can comprise any percarboxylic acid, particularly water-soluble percarboxylic acids and especially is selected from low or medium molecular weight aliphatic percarboxylic acids such as those containing up to 9 carbons. The invention will be described with particular reference to peracetic acid, but for example, perpropionic acid may be employed instead of or together with peracetic acid.

The concentration of peracid in preformed compositions intended for storage and/or transportation can be selected over a wide range, such as from about 0.01% to 40% w/w. In many embodiments, the compositions comprise a dilute solution of the peracid, such as from about 0.5% to about 10% w/w. The actual selection of the peracid is often a matter at the discretion of the producer, for his own convenience, balancing the beneficial and disadvantageous effects of a chosen concentration. Concentrations of around 2 to 3%

w/w peracid and from about 4 to about 5.5% w/w peracid are quite popular as compromises that are readily transportable without transporting too much water. The weight ratio of nonionic surfactant to peracid is often selected to be in the range of from 10:1 to 1:5, and preferably from 4:1 to 1:1.

In many desirable compositions according to the present invention, which are intended for storage and or transportation, the peracid is made by a reaction between the corresponding carboxylic acid or carboxylic acid anhydride and hydrogen peroxide in an aqueous medium. It is particularly desirable to employ compositions in which the peracid is present at a concentration that is substantially in equilibrium with residual concentrations of its corresponding carboxylic acid and hydrogen peroxide. In such compositions, the concentration of hydrogen peroxide is often selected in the range of from about 0.1 to 30% w/w and the concentration of carboxylic acid from about 0.5 to about 50% w/w. In practice, the weight ratio of carboxylic acid e.g. acetic acid or hydrogen peroxide relative to the peracid can be varied at the discretion of the producer/user within the entire range, provided that an appropriate concentration of the other reagent is present. In general terms, for a stable equilibrium, a low peroxide concentration is balanced by a high carboxylic acid concentration, and vice versa, and ratio of peroxide plus carboxylic acid to peracid increases as the concentration of peracid decreases. For many dilute, transportable peracid compositions containing less than 6% peracid, and often greater than 1% peracid, the weight ratio of peroxide to peracid and of carboxylic acid to peracid are each often selected in the range of from about 1:10 to about 10:1.

The transportable compositions can be employed neat, for example in the disinfection of hard surfaces such as work surfaces, equipment or sanitary ware, particularly if they contain less than 6% peracid, but they are often diluted with water before use or it is an aqueous medium which it is intended to disinfect. The extent of dilution is at the discretion of the user, taking into account the extent and nature of the infecting micro-organisms which it is desired to kill, the period available for the kill and the operational conditions such as the temperature. Where the disinfection process involves a manual treatment stage, for example, distributing a composition over a hard surface with a cloth, it is often desirable that the peracid concentration in the solution in use is less than about 0.1%.

It is convenient to express the concentration of the disinfectant composition by reference to the concentration of the peracid. The alkoxylated alcohol is present at a relative concentration thereto as indicated previously herein. The peracid concentration is usually at least 5 mg/l and often up to 1000 mg/l. For a number of micro-organisms, a concentration of between 25 and 400 mg/l is selected. Depending on the conditions, though, for shock treatments, peracid concentration of above 1000 mg/l, for example up to about 10000 mg/l can be contemplated and for prolonged contact, a concentration of 1 to 5 mg/l peracid can sometimes be appropriate.

It will be recognized that the advantage of the invention composition, compared with prior disclosed compositions not containing the alkoxylated alcohol, is that it is relatively more effective at approximately neutral or mildly alkaline compositions, and especially at a pH of from above 6 to 8. The user can obtain the benefit of a similar extent of disinfection using a peracid composition, such as peracetic acid at a higher pH, i.e. avoiding or reducing the extent of pH adjustment, or alternatively he can obtain improved disinfection if he chooses not to acidify.

In theory, microbicidal compositions can contain other active microbicides in order to augment the activity from peracids, but there can be no guarantee that the addition of further components will improve the overall microbicidal effectiveness. Some combinations of peracid with other components are unstable and others show little or no detectable change in performance, at least with reference to various widespread target micro-organisms.

One such class of other microbicides comprises quaternary ammonium compounds, a class of carbonic surfactants. They are widely available, and hence are attractive, but there can be difficulties associated with their use. Within the spectrum of micro-organisms that it is desired to control, i.e. kill or inactivate, by the application of a microbicidal composition are bacteria. Bacteria themselves are generally divided into two classes, gram-negative and gram-positive bacteria. It is generally recognized that, of the two classes, gram-positive bacteria are, in many cases, relatively easy to control by the application of quaternary ammonium compounds, but that gram negative bacteria are much more resistant to them. It is particularly desirable to control gram negative bacteria, because the group comprises many well known pathogens, for example, many species of faecal bacteria, pseudomonads which can cause skin irritation, and other species of bacteria, such as salmonella which can cause food poisoning. Self-evidently, it would be advantageous to identify microbicidal compositions having improved activity against gram negative bacteria.

It has been found to be especially desirable to employ the combination of peracid and alkoxylated alcohol in conjunction with a quaternary ammonium cationic surfactant, since by so doing, the resultant three component combination has been shown to be particularly effective against gram negative bacteria. The quaternary ammonium compound, which can be represented by the general formula  $R^aR^bR^cR^dN^+Q^-$  in which substituents  $R^a$ ,  $R^b$ ,  $R^c$ , and  $R^d$  each represent an alkyl or aryl group or two of which combine with the nitrogen to form a heterocyclic nucleus, the total number of carbons in  $R^a$  to  $R^d$  normally comprising from about 10 to about 30 carbons. One or two of the substituents normally contains from 8 to 18 linear carbons often from C12 to C16, or forms part of the heterocyclic nucleus such pyridinium. One of the substituents can conveniently comprise a benzyl group. The remaining substituents usually are selected from C1 to C4 alkyl groups, and especially methyl or ethyl. Q represents a counterion such as hydroxyl, sulphate or alkyl sulphate.

The quaternary ammonium cationic surfactant (QACS) is often incorporated at a relatively small proportion of the overall composition, such as up to about 5% w/w in a dilutable composition, or up to about 0.5% w/w in a composition ready for use without further dilution. It will be recognised that in a two pack system, the QACS can be incorporated in either or both of the solutions at a concentration selected accordingly.

A particularly effective range of compositions comprises peracetic acid at a weight concentration in the region of about 2.0 to 5.5%, preferably in the presence of sufficient hydrogen peroxide and acetic acid selected together in the ranges of 1 to 20% and 1 to 50% respectively to obtain an equilibrium composition, from 4 to 15% alkoxylated alcohol and from 0.05 to 0.5% QACS. Such compositions may often be diluted by a factor in the range of from about 10 to about 1000, depending on the peracid concentration before dilution and its desired concentration for disinfection.

The invention compositions are particularly intended for use in the food, beverage and allied industries. The beverage

industries include brewing, wine-making and alcohol distillation, and in dairies. In such industries, it is especially important to guard against the contamination of food and drink intended not only for human consumption, but also that intended for consumption by livestock, and pets. In such industries, the compositions can be used to disinfect brewing vessels, or surfaces that come into contact with prepared food or drink which in normal circumstances would be consumed without cooking. Those surfaces can include food mixing or washing vessels, transport equipment such as conveyors, arid filling and packaging equipment. Compositions for use in these industries generally contain or are diluted in uses to peracid concentrations of below 500 mg/l with corresponding concentrations of the other constituents. Such diluted compositions in practice are rarely non-equilibrium in that over a period of time there would be a tendency for the peracid to re-equilibrate to hydrogen peroxide and carboxylic acid, but that is acceptable under disinfection treatment times. The use of the two component composition enables the process to be effected often without any pH alteration, and the use of the three component composition is especially desirable in that it combines the advantage of the two component combination with that of a wider spectrum activity, even at approximately neutral or alkaline pH.

The compositions according to the present invention can be prepared by mixing a first solution comprising a peracid, with a second solution comprising an ethoxylated and propoxylated alcohol nonionic surfactant according to the general chemical formula (1):



wherein R represents an alkyl group of at least 6 carbon atoms n and p each represent an integer.

Having described the invention in general terms, specific embodiments thereof will be described hereinafter in greater detail by way of non-limiting example only.

#### Comparisons CA to CD and Examples 1 and 2

In Comparison CA, the treatment employed was a dilutable grade of peracetic acid commercially available from Solvay Interlox Limited under the Trade Mark PROXITANE, containing 5% peracetic acid, 10% w/w acetic acid and 20% w/w hydrogen peroxide, diluted to give an in use concentration of peracid of 50 mg/l for the bacteria, and 200 mg/l for the yeast.

In Comparison CB, the treatment employed comprised 0.2% w/v active ingredient of a quaternary ammonium cationic surfactant (QACS) available from Albright and Wilson under their Trade Mark EMPIGEN grade CM.

In Comparison CC, the composition employed comprised a solution of 10% w/v of an ethoxylated/propoxylated linear primary alcohol (alkoxylated alcohol) available from Union Carbide under their Trade Mark TRITON grade DF16.

In Comparison CD, the treatment employed was as in Comparison CA, except that 0.2% w/v active ingredient of the QACS of Comparison CB was also employed.

In Example 1, the treatment employed was as for Comparison CA, except that 10% w/v of the (alkoxylated alcohol) of Comparison CC was also employed.

In Example 2, the treatment employed was as for Example 1, except that 0.2% w/v active ingredient of the QACS of Comparison CB was also employed.

The effectiveness of each of the various Comparison and Example compositions as a microbicide was determined against three microbes considered to be representative for beverage industries, namely a yeast, *Candida albicans*, a gram negative bacterium, *Pseudomonas aeruginosa*, and a Gram-positive bacterium, *Staphylococcus aureus*.

The effectiveness of the composition as a microbicide was tested in a disinfectant suspension test. The microbicide was challenged with an inoculum of the microbe containing a measured concentration of between  $1 \times 10^5$  to  $3 \times 10^8$  cfu for bacteria and between  $1 \times 10^7$  and  $3 \times 10^7$  cfu for the yeast in the presence of yeast extract (0.4%) and standard hard water for a period of 5 minutes at ambient temperature. The composition was quenched in the standard manners for peracid and surfactants depending on which components are present and thereafter determining the number of viable micro-organisms by conventional plate culture techniques. The studies were conducted in duplicate.

The number of surviving viable bacteria or yeasts per unit volume (cfu) was then compared with the number before the disinfection treatment began, and the result given is the fraction that had been killed, expressed a logarithm, base 10; the higher the resultant number, the more effective the disinfection. The maximum for the yeast was 4.6, for the gram -ve bacterium was 6.3 and 5.9 for the Gram +ve bacterium.

The results of the disinfection studies are summarized in Table 1 below

TABLE 1

Measured Log Reduction Factor for				
Trial	pH	Yeast	Gram -ve Bacteria	Gram +ve Bacteria
CA	4	4.5	6.3	5.9
	6	3.3	3.5	4.4
	8	1.8	2.3	1.7
CB	10	0.3	1.4	0.6
	4	0.4	3.8	5.9
	6	0.7	0	5.9
CC	8	3.4	0	5.9
	10	4.6	0	5.9
	4	0.5	1.9	1.8
CD	6	0.7	0	0.7
	8	0.6	0	0.9
	10	0.6	0	1.1
Ex 1	4	4.6	6.3	5.9
	6	4.6	3.5	5.9
	8	4.6	2.3	5.9
Ex 2	10	4.6	1.1	5.9
	4	4.6	6.3	5.9
	6	4.1	6.3	5.9
Ex 2	8	2.9	4.9	5.0
	10	0.6	1.9	1.9
	4	3.1	6.3	5.9
	6	0.6	6.3	5.9
	8	4.6	6.3	5.9
	10	4.5	2.5	4.5

From Table 1, it can be seen in Comparison CA that the effectiveness of peracetic acid as a microbicide is very good at acidic pHs of the region of pH 4, but that its effectiveness diminishes as the pH of the solution containing the yeast or bacterium increases. A comparison of Comparisons CA with CB and CD shows that the QACS complements the peracetic acid in terms as the pH varies through the range tested for the yeast, without demonstrating synergism, but that there is no complementary action for the bacteria. A comparison of Comparisons CA, CC and Example 1 demonstrates that the combination of the alkoxylated alcohol and peracetic acid offers similar performance to that of peracetic acid alone, at

the low pH, and at higher pHs of from pH 6 to pH 10 shows synergism especially for the Gram negative bacteria which are resistant to QACS. Thus, Table 1 shows that the pH range in which peracids retain their effectiveness is visibly extended from about pH 4 without the alkoxyated alcohol up as high as about pH 8 with the alkoxyated alcohol. Table 1 also shows complementary results or synergistic results for the Gram positive bacteria and the yeast at the higher pHs.

From a comparison of Examples 1 and 2, it can be seen that the addition of the QACS is beneficial at the high end of the pH range, and particularly at about pH 8, complementing the other components and producing a composition that is especially effective for all three of the test micro-organisms.

#### Storage Stability Trial

To 247.5 g of a sample of peracetic acid commercially available from Solvay Interrox Limited under the Trade Mark PROXITANE, containing 5% peracetic acid, 10% w/w acetic acid and 20% W/w hydrogen peroxide was added 0.11 g of a quaternary ammonium cationic surfactant (QACS) available from Albright and Wilson under their Trade Mark EMPIGEN grade CM and 2.39 g of an ethoxylated/propoxylated linear primary alcohol (alkoxyated alcohol) available from Union Carbide under their Trade Mark TRITON grade DF16. After 160 days storage at ambient temperature (ca. 20°-25° C.), analysis of the sample showed that 95% of the peracetic acid was retained, indicating that the sample had excellent storage stability.

We claim:

1. An acidic, storage stable peracid disinfectant solution comprising an aqueous solution comprising an amount effective for disinfection of an aliphatic peracid containing up to 9 carbon atoms and an ethoxylated and propoxylated alcohol nonionic surfactant according to the general formula:



wherein R represents an alkyl group of at least 6 carbon atoms and n and p each represent an integer.

2. A solution according to claim 1, wherein the nonionic surfactant and peracid are present in a weight ratio within the range of from 10:1 to 1:5.

3. A solution according to claim 2, wherein the nonionic surfactant and peracid are present in a weight ratio within the range of from 4:1 to 1:1.

4. A solution according to any one of claims 1, 2, or 3, wherein the solution contains from about 1 to about 6% w/w peracid.

5. A solution according to any one of claims 1, 2 or 3, wherein the peracid comprises peracetic acid.

6. A solution according to claim 5, wherein the solution comprises from 1 to 6% w/w peracetic acid.

7. A solution according to any one of claims 1, 2, 3 or 6, wherein the solution contains up to 0.5% w/w of a quaternary ammonium cationic surfactant.

8. In a process for disinfection of a substrate, in which the substrate is contacted with a disinfectant solution, the improvement wherein the disinfectant solution comprises an aqueous solution comprising an amount effective for disinfection of an aliphatic peracid containing up to 9 carbon atoms and an ethoxylated and propoxylated alcohol nonionic surfactant according to the general formula:



wherein R represents an alkyl group of at least 6 carbon atoms and n and p each represent an integer.

9. A process according to claim 8, wherein the nonionic surfactant and peracid are present in a weight ratio within the range of from 10:1 to 1:5.

10. A process according to claim 7, wherein the nonionic surfactant and peracid are present in a weight ratio within the range of from 4:1 to 1:1.

11. A process according to claim 8, wherein the aliphatic peracid comprises from 1 to 6% w/w peracetic acid.

12. A process according to any one of claims 8, 9, 10 or 11, further comprising diluting the solution.

13. A process according to any one of claim 8, 9, 10 or 11, wherein disinfection is effected without diluting the solution.

14. A process according to claim 8, 9, 10 or 11, wherein the process is carried out at a pH of at least 6.

15. A process according to claim 8, wherein the solution contains up to 0.5% w/w of a quaternary ammonium cationic surfactant.

16. A process according to claim 8, wherein the process is carried out at a pH of from pH 6 to 8.

17. A process for preparing an aqueous storage stable disinfectant solution which comprises mixing an aqueous solution comprising an aliphatic peracid containing up to 9 carbon atoms with a solution comprising an ethoxylated and propoxylated alcohol nonionic surfactant according to the general formula:



wherein R represents an alkyl group of at least 6 carbon atoms and n and p each represent an integer.

\* \* \* \* \*

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US005624634A

**United States Patent** [19]  
**Brougham et al.**

[11] **Patent Number:** **5,624,634**  
[45] **Date of Patent:** **\*Apr. 29, 1997**

- [54] **PERACID COMPOSITIONS FOR MEDICAL DISINFECTION**
- [75] **Inventors:** Paul Brougham, Rainhill; Robert A. Simms, Warrington, both of United Kingdom
- [73] **Assignee:** Solvay Interlox Limited, Cheshire, United Kingdom
- [\*] **Notice:** The term of this patent shall not extend beyond the expiration date of Pat. No. 5,545,343.
- [21] **Appl. No.:** 458,902
- [22] **Filed:** Jun. 2, 1995

**Related U.S. Application Data**

- [62] **Division of Ser. No. 211,659, Jun. 21, 1994, Pat. No. 5,545,343.**
- [30] **Foreign Application Priority Data**  
Oct. 17, 1991 [GB] United Kingdom ..... 9122048
- [51] **Int. CL<sup>6</sup>** ..... A01N 59/00
- [52] **U.S. CL** ..... 422/28; 514/557; 252/387; 252/389.2; 252/186.26; 510/372
- [58] **Field of Search** ..... 422/28, 32, 37, 422/61; 562/3, 4, 6; 252/142, 95, 97, 173, 387, 389.2, 357, 186.26; 514/557; 510/372

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[57] **ABSTRACT**

A multi-component product for providing, on mixing of the components, a disinfectant composition. A first component of the product comprises an aqueous solution of a lower aliphatic peracid and a second component comprises an aqueous solution containing a phosphate corrosion inhibitor and either a hydrogen peroxide stabilizer, a peracid stabilizer, or both.

**48 Claims, No Drawings**

# PERACID COMPOSITIONS FOR MEDICAL DISINFECTION

This is a division of application Ser. No. 08/211,659 filed Jun. 21, 1994, now U.S. Pat. No. 5,545,343.

This invention concerns compositions, processes for the preparation of such compositions, two-pack systems for preparing such compositions and uses of such compositions. More particularly the present invention concerns compositions comprising dilute aqueous solutions of lower aliphatic peracids and their use as disinfectant compositions.

The lower aliphatic peracids are effective wide-spectrum bactericides which have the particular advantage, in use, of leaving as residues only the corresponding lower aliphatic acids and therefore being particularly suitable for applications which require a non-environmentally-polluting disinfectant. While the lower aliphatic peracids in general are contemplated herein, for example those corresponding to carboxylic aliphatic acids containing 2 to 9 carbon atoms, peracetic acid is particularly envisaged since it is already a commercially important peracid for disinfectant purposes. Where the following description relates to peracetic acid it is to be understood that the other peracids may be read in substitution therefor provided that the technical context allows it.

Aqueous solutions of peracetic acid containing up to about 45% by weight of peracetic acid are commercially available. Such solutions may be produced by reacting appropriately concentrated hydrogen peroxide and acetic acid in an aqueous medium in the presence of an acid catalyst which is usually sulphuric acid or other strong mineral acid. The acid catalyst may be present in from about 0.1% to about 5% by weight of the reaction mixture.

Aqueous solutions of peracetic acid represent equilibrium mixtures of the reactants and the reaction products and, under relatively forcing reaction conditions, for example when using one or more of a substantial quantity of catalyst, an elevated reaction temperature and a concentrated reaction mixture, equilibrium may be substantially reached in a relatively short time. When using the strong acid catalyst in from 2% to 5% of the reaction mixture, a temperature of from 30° C. to 50° C. and a concentration of acid above about 20% by weight the reaction mixture may come to equilibrium within hours. For some applications, or where long storage is envisaged, it may not be desirable for there to be catalyst residues in a peracid product particularly, for example, dilute products intended for personal or domestic hygiene use. For many applications dilute solutions of peracetic acid, for example below 5% by weight but often below 2%, for example from 0.1% to 2% by weight, are required. Concentrations of peracetic acid above 0.5% by weight for example from 0.5% to 1% by weight, are particularly effective bactericidally in, for example, toilet cleansing applications. Such dilute peracetic acid solutions may be produced directly by reacting acetic acid and hydrogen peroxide in a suitably dilute reaction medium but equilibrium can take an extremely long time to reach, particularly at the more extreme dilutions envisaged. At peracid concentrations below 1% by weight equilibrium may take a month or more to reach if the reaction is not acid catalyzed or a week or more even if the reaction is acid catalyzed. This entails a very heavy utilization of plant and equipment on a large production scale.

If a concentrated equilibrium solution of peracetic acid is diluted with water the equilibrium point of the system is progressively altered, as dilution progresses, in favour of the regeneration of the original reactants. The ageing time taken

to attain the new equilibrium point, after dilution, is of a similar order to that required to produce such a dilute solution directly from suitable reactants. Such a diluted solution may be used directly although it is not at equilibrium and is therefore of variable composition in storage. Such non-equilibrium diluted solutions also have a composition dictated by the equilibrium point applying at the original concentration, which may not be desired in some applications.

In 1955 Greenspan et al. (Proc. 42nd Ann. Mtg. Chem. Spec. Man. Ass. December 1955), disclosed that stable dilute peracetic acid solutions can be prepared by the use of peracid stabilizers in conjunction with proper adjustment of the relative concentrations of the components of the dilute peracid solution, that is to say that, if the prepared dilute solution is not fully at equilibrium, adjustment of the balance of the components can achieve stability. The solutions in question may be prepared by dilution of commercial, e.g. fully equilibrated peracetic acid which has been produced by the use of small amounts of a mineral acid catalyst.

U.S. Pat. No. 4,297,298 describes the production of an aqueous solution of a lower aliphatic peracid by preparing in a first process step a concentrated solution of the peracid from the corresponding carboxylic acid or anhydride and concentrated hydrogen peroxide in the presence of a small quantity of a strong acid catalyst and diluting the solution with a solution containing at least one of the reagents from the first process step so as to bring the concentration of the aliphatic peracid to the rated concentration of the mixture the concentration of the diluent reagent or reagents being chosen "so that once dilution has been brought about, the system is no longer at equilibrium, but tends to move in the direction of forming further aliphatic peracid at a very slow rate." The process specifically described in U.S. Pat. No. 4,297,298 produces a non-equilibrium composition which contains an extremely high concentration of hydrogen peroxide, e.g. from 28% to 46%. Such a concentration on contact with the user would cause skin bleaching and pain.

U.S. Pat. No. 4,743,447 describes the production of solutions having a hydrogen peroxide base for disinfecting contact lenses, the solution having from 0.005% to 0.1% by weight of peracetic acid, 1% to 8% by weight of hydrogen peroxide and sufficient acetic acid for the system to reach equilibrium. Such a solution may be prepared by direct reaction using a very dilute reaction mixture with lengthy equilibration or from a stable commercial solution having a "weak concentration" of peracetic acid to which the other constituents of the composition are added. This teaching does not therefore avoid the separate initial step of producing a stable weak solution of peracetic acid from which to produce in turn the final product.

EP-A-0357238 (Steris Corp) discloses an anti-microbial composition comprising a strong oxidant, a copper and brass corrosion inhibitor, a buffering agent, at least one anti-corrosive agent which exhibits corrosion inhibition in at least aluminium, carbon steel and stainless steel, and a wetting agent. The corrosion inhibitors specifically disclosed for brass and aluminium comprise triazoles and molybdates, which are known to have unfavourable toxicity, and which therefore renders undesirable their use in a medical environment.

It is an object of the present invention to provide a disinfectant composition, based on a dilute solution of peracid, which may be used on medical equipment comprising metal components to be disinfected.

In accordance with the present invention there is provided a process for the preparation of an aqueous disinfectant



tant composition characterized in that the process comprises mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising a corrosion inhibitor and a hydrogen peroxide stabilizer and/or peracid stabilizer.

In another aspect, the present invention provides a disinfectant composition obtainable by a process comprising mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising a corrosion inhibitor and a hydrogen peroxide stabilizer and/or peracid stabilizer. It is to be understood that the peracid composition of the present invention is not in equilibrium and comprises a relatively higher concentration of stabilizer (s) than a skilled person would expect to find in a composition which is in equilibrium and comprises a similar concentration of peracid.

In yet another aspect, the present invention provides a two-pack system for the preparation of a disinfectant composition, characterized in that one pack comprises a first aqueous solution comprising a lower aliphatic peracid, and the other pack comprises a second aqueous solution comprising a corrosion inhibitor and a hydrogen peroxide stabilizer and/or peracid stabilizer.

The first aqueous solution preferably comprises a lower aliphatic peracid, such as peracetic acid, in an amount of from 2% to 10%, more preferably from 3% to 7%, by weight of the solution. The first aqueous solution may additionally comprise stabilizer(s) for the hydrogen peroxide and/or the peracid in the equilibrium solution, each relevant stabilizer being present in a preferred amount of from 20 to 10,000 ppm. Preferably both the peroxide and peracid are stabilized in the solution, giving a preferred combined stabilizer concentration of from 3000 to 6000 ppm. A suitable peracid stabilizer is dipicolinic acid and suitable peroxide stabilizers include phosphonic acids and salts thereof, e.g. the products sold by Monsanto under the trade mark "DEQUEST" such as hydroxyethylidenediphosphonate, diethylenetriamine-pentamethylene phosphonate and ethylenediaminetetraethylene phosphonate and those stabilizers claimed in European patent application 0426949, especially cyclohexane-1,2-diaminetetramethylenephosphonic acid and salts thereof (CDTMP). It should be understood that the first solution is usually an equilibrium mixture of the relevant reactants and reaction products, as generally described in the paragraph bridging page 1 and page 2 above, and that the above specified amount of peracid indicates the amount of peracid *per se* in the solution. A preferred process for the preparation of dilute solutions of lower aliphatic peracids useful in the present invention is disclosed in PCT Patent Application No. WO 91/13058.

The second aqueous solution preferably comprises from 0.1% to 5%, more preferably from 0.1% to 1%, by weight of the solution of a corrosion inhibitor. Preferably, the corrosion inhibitor is an alkali metal phosphate, most preferably a potassium phosphate. Dipotassium hydrogen orthophosphate ( $K_2HPO_4$ ) is the most preferred corrosion inhibitor.

The second aqueous solution preferably comprises from 0.1% to 2%, often 0.1% to 1%, more preferably from 0.2% to 0.7% or 0.7% to 1%, by weight of the solution of hydrogen peroxide stabilizer and/or peracid stabilizer, such as about 0.5% or about 1% stabilizer. Preferably a hydrogen peroxide stabilizer is used. The preferred peroxide stabilizers are phosphonic acids and salts thereof, for example, those described hereinabove as suitable for the first aqueous solution. A suitable peracid stabilizer is dipicolinic acid.

Mixing of the first and second solutions give a disinfectant composition immediately after mixing comprising at

least 0.05% and generally not greater than 1% by weight peracid. In many embodiments, the mixture of the two solutions immediately after mixing comprises from 0.1% to 0.25% or from 0.25% to 0.5% by weight peracid. The mixture also desirably comprises from 0.1% to 5% corrosion inhibitor and from 0.1% to 1% peroxide stabilizer and/or peracid stabilizer. Such mixtures can often be obtained conveniently by selecting a volume ratio of the first solution to the second solution which is often at least 1:5 and not usually greater than 1:50, preferably from 1:10 to 1:30, taking into account the concentration of the components in each solution.

One or both of the aqueous solutions may contain other components useful in disinfectant compositions, e.g. a triazole corrosion inhibitor and/or a wetting agent, though the presence of these components is not essential to obtain the advantages of the invention (indeed, such components may be slightly detrimental). One or both of the solutions may contain an indicator which undergoes a colour change to indicate that the two solutions have been mixed together.

It will be appreciated that the compositions provided by the process of the present invention are not in equilibrium and that in the natural course of events the peracid component of the composition will tend towards equilibrium. For example, the composition described in the paragraph immediately above this paragraph will begin to change within a relatively short period of time from mixing the first and second solutions together and that as time passes the peracid concentration in the solution will reduce as it tends towards equilibrium. Normal equilibrium could be expected to be reached after about two days, assuming the peracid and/or peroxide does not decompose in that period.

The compositions of the present invention are particularly suitable for use as medical disinfectants. Preferably, the compositions are used to disinfect medical equipment which has metal, e.g. aluminum, brass, copper and especially steel, components required to be disinfected. For example, the composition is particularly useful for disinfection of endoscopes. The present invention may have a further advantage over the prior art compositions of Steris. The selected components of the invention composition interact to protect metal components, especially steel components, with regard to localized corrosion, e.g. pitting, as well as, if not better than, if molybdate, triazole and/or wetting agent were present. This is most surprising in light of the disclosure on page 4, lines 7 to 9, of Steris.

The present invention has the advantage of providing a dilute composition comprising a relatively high concentration of peracid. Furthermore, the process of the present invention enables a relatively longer shelf life for the separate aqueous solution than would be achieved if the composition was supplied *per se*.

The invention will now be further described, without limitation, with reference to the following examples:

#### EXAMPLE 1

Preparation of Composition according to the Present Invention

A two-pack system was prepared. One pack contained 250 ml of an aqueous peracetic acid, 5% (active) by weight, solution. The other pack contained 10 l of an aqueous solution comprising 0.6% by weight dipotassium hydrogen ortho phosphate and 0.5% by weight CDTMP. The two packs were then mixed together to form a composition of the present invention.

## EXAMPLE 2

Preparation of Composition according to the Present Invention

A solution of 5% w/w peracetic acid, 20% w/w hydrogen peroxide, 8% w/w acetic acid was diluted 14 times with a solution containing 1% w/w CDTMP and 0.8% dipotassium hydrogen orthophosphate to form a solution containing 3,500 ppm peracetic acid.

## EXAMPLE 3 AND COMPARISON A

## Corrosion Trials for Disinfectant Compositions

Duplicate coupons of mild steel and stainless steel 316 were immersed for 72 hours at room temperature (15°-25° C.) in disinfectant solutions. In Example 3, the disinfectant solution was prepared according to the method of Example 2 after a dilution by 25 times to produce a solution containing 2000 ppm peracetic acid. In Comparison A, the disinfectant solution was prepared according to the example given in the first table, page 6, lines 1 to 18 of European Patent Application No 0 357 238. The solutions were completely replaced daily with fresh solutions. Examination of the coupons with both the naked eye and an optical microscope on completion of the trial showed that for both of the metals in the composition according to the Steris Application, there was significant localized corrosion and pitting on the metal but for the metals in the disinfectant solution according to the present invention there was only very slight localized corrosion.

The significant reduction in localized corrosion achieved with compositions according to the present invention is surprising given the disclosure on page 4, lines 7 to 9 of the Steris Application, and is particularly advantageous because the results were achieved without the use of any toxic molybdate and triazole.

We claim:

1. A method for the preparation of an aqueous disinfectant composition comprising mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising a phosphate corrosion inhibitor and at least one peroxide stabilizer selected from the group consisting of hydrogen peroxide stabilizers and peracid stabilizers.

2. A method as claimed in claim 1 wherein the first aqueous solution comprises a ( $C_1-C_9$ ) aliphatic peracid in an amount of from 2% to 10% by weight of the first aqueous solution.

3. A method as claimed in claim 1 wherein the first aqueous solution comprises a ( $C_1-C_9$ ) aliphatic peracid in an amount of from 3% to 7% by weight of the first aqueous solution.

4. A method as claimed in claim 1 wherein the first aqueous solution comprises peracetic acid.

5. A method as claimed in claim 1 wherein the corrosion inhibitor comprises an alkali metal phosphate.

6. A method as claimed in claim 1 wherein the corrosion inhibitor comprises dipotassium hydrogen orthophosphate.

7. A method as claimed in claim 1 wherein the second aqueous solution comprises from 0.1% to 5% by weight of the second aqueous solution of said corrosion inhibitor.

8. A method as claimed in claim 1 wherein the second aqueous solution comprises from 0.1% to 1% by weight of the second aqueous solution of said corrosion inhibitor.

9. A method as claimed in claim 1 wherein the second aqueous solution comprises from 0.1% to 2% by weight of the second aqueous solution of said at least one peroxide stabilizer.

10. A method as claimed in claim 9 wherein the second aqueous solution comprises from 0.2% to 0.7% by weight of the second aqueous solution of, said at least one peroxide stabilizer.

11. A method as claimed in claim 9 wherein the second aqueous solution comprises from 0.7% to 1% by weight of the second aqueous solution of said at least one peroxide stabilizer.

12. A method as claimed in claim 1 wherein the peroxide stabilizer is only hydrogen peroxide stabilizer.

13. A method as claimed in claim 1 wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:5 to 1:50.

14. A method as claimed in claim 1 wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:10 to 1:30.

15. A method as claimed in claim 1 wherein one or both of the two aqueous solutions comprises an indicator which undergoes a color change when the solutions are mixed together.

16. A method of disinfecting an object which comprises: mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising a phosphate corrosion inhibitor and at least one peroxide stabilizer selected from the group consisting of hydrogen peroxide stabilizers and peracid stabilizers to produce an aqueous disinfectant solution; and contacting an object to be disinfected with said aqueous disinfectant solution for a time sufficient to disinfect the object.

17. A method as claimed in claim 16 wherein the first aqueous solution comprises a ( $C_1-C_9$ ) aliphatic peracid in an amount of from 2% to 10% by weight of the first aqueous solution.

18. A method as claimed in claim 16 wherein the first aqueous solution comprises a ( $C_1-C_9$ ) aliphatic peracid in an amount of from 3% to 7% by weight of the first aqueous solution.

19. A method as claimed in claim 16 wherein the first aqueous solution comprises peracetic acid.

20. A method as claimed in claim 16 wherein the corrosion inhibitor comprises an alkali metal phosphate.

21. A method as claimed in claim 16 wherein the corrosion inhibitor comprises dipotassium hydrogen orthophosphate.

22. A method as claimed in claim 16 wherein the second aqueous solution comprises from 0.1% to 5% by weight of the second aqueous solution of said corrosion inhibitor.

23. A method as claimed in claim 16 wherein the second aqueous solution comprises from 0.1% to 1% by weight of the second aqueous solution of said corrosion inhibitor.

24. A method as claimed in claim 16 wherein the second aqueous solution comprises from 0.1% to 2% by weight of the second aqueous solution of said at least one peroxide stabilizer.

25. A method as claimed in claim 16 wherein the second aqueous solution comprises from 0.2% to 0.7% by weight of the second aqueous solution of said at least one peroxide stabilizer.

26. A method as claimed in claim 16 wherein the second aqueous solution comprises from 0.7% to 1% by weight of the second aqueous solution of said at least one peroxide stabilizer.

27. A method as claimed in claim 16 wherein the peroxide stabilizer is only hydrogen peroxide stabilizer.

28. A method as claimed in claim 16 wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:5 to 1:50.

29. A method as claimed in claim 16 wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:10 to 1:30.

30. A method as claimed in claim 16 wherein one or both of the two aqueous solutions comprises an indicator which undergoes a color change when the solutions are mixed together.

31. A method as claimed in claim 16 wherein said object comprises a metal component of medical equipment.

32. A method as claimed in claim 31 wherein said medical equipment comprises an endoscope.

33. A multi-component product for providing, on mixing of the components, a disinfectant composition, said product comprising a first component which comprises a first aqueous solution comprising a lower aliphatic peracid, and a second component which comprises a second aqueous solution comprising a phosphate corrosion inhibitor and at least one peroxide stabilizer selected from the group consisting of hydrogen peroxide stabilizers and peracid stabilizers.

34. A product as claimed in claim 33 wherein the first aqueous solution comprises a ( $C_2-C_9$ ) aliphatic peracid in an amount of from 2% to 10% by weight of the first aqueous solution.

35. A product as claimed in claim 33 wherein the first aqueous solution comprises a ( $C_7-C_9$ ) aliphatic peracid in an amount of from 3% to 7% by weight of the first aqueous solution.

36. A product as claimed in claim 33 wherein the first aqueous solution comprises peracetic acid.

37. A product as claimed in claim 33 wherein the corrosion inhibitor comprises an alkali metal phosphate.

38. A product as claimed in claim 33 wherein the corrosion inhibitor comprises dipotassium hydrogen orthophosphate.

39. A product as claimed in claim 33 wherein the second aqueous solution comprises from 0.1% to 5% by weight of the second aqueous solution of said corrosion inhibitor.

40. A product as claimed in claim 33 wherein the second aqueous solution comprises from 0.1% to 1% by weight of the second aqueous solution of said corrosion inhibitor.

41. A product as claimed in claim 33 wherein the second aqueous solution comprises from 0.1% to 2% by weight of the second aqueous solution of said at least one peroxide stabilizer.

42. A product as claimed in claim 33 wherein the second aqueous solution comprises from 0.2% to 0.7% by weight of the second aqueous solution of said at least one peroxide stabilizer.

43. A product as claimed in claim 33 wherein the second aqueous solution comprises from 0.7% to 1% by weight of the second aqueous solution of said at least one peroxide stabilizer.

44. A product as claimed in claim 33 wherein the peroxide stabilizer is only hydrogen peroxide stabilizer.

45. A product as claimed in claim 33 wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:5 to 1:50.

46. A product as claimed in claim 45 wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:10 to 1:30.

47. A product as claimed in claim 33 wherein one or both of the two aqueous solutions comprises an indicator which undergoes a color change when the solutions are mixed together.

48. A product according to claim 33 wherein said phosphate corrosion inhibitor is a steel corrosion inhibitor.

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US005720983A

# United States Patent [19]

Malone

[11] Patent Number: 5,720,983

[45] Date of Patent: \*Feb. 24, 1998

[54] TWO PACK PERACID DISINFECTION SYSTEM, METHOD OF PREPARATION OF DISINFECTANT COMPOSITION THEREFROM, AND USE THEREOF IN DISINFECTING A SURFACE

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[21] Appl. No.: 481,323

[22] PCT Filed: Jan. 5, 1994

[\*] Notice: The term of this patent shall not extend beyond the expiration date of Pat. Nos. 5,545,323 and 5,624,634.

[86] PCT No.: PCT/GB94/00010

§ 371 Date: Jul. 5, 1995

§ 102(e) Date: Jul. 5, 1995

[87] PCT Pub. No.: WO94/15465

PCT Pub. Date: Jul. 21, 1994

[30] Foreign Application Priority Data

Jan. 9, 1993 [GB] United Kingdom ..... 9300366

[51] Int. Cl.<sup>6</sup> ..... A01N 37/16; A01N 25/22;  
A01N 59/00; A61L 2/18

[52] U.S. Cl. .... 424/616; 424/613; 424/126;  
514/557; 514/558; 514/560; 514/970; 422/28;  
252/186.26; 252/387; 252/389.2

[58] Field of Search ..... 514/557, 558,  
514/560, 970; 424/616, 613, 126; 422/28;  
252/186.26, 387, 389.2

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[57] ABSTRACT

An aqueous composition comprising a lower aliphatic peracid, a corrosion inhibitor and a peroxide stabilizer and/or peracid stabilizer, is useful for disinfecting medical equipment, particularly metal components of such equipment. A process for obtaining such compositions is also provided and comprises mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising hydrogen peroxide, a corrosion inhibitor and a hydrogen peroxide stabilizer and/or a peracid stabilizer. The first and second aqueous solutions can form a two pack system for obtaining such compositions.

43 Claims, No Drawings

CIP 634

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## TWO PACK PERACID DISINFECTION SYSTEM, METHOD OF PREPARATION OF DISINFECTANT COMPOSITION THEREFROM, AND USE THEREOF IN DISINFECTING A SURFACE

This application is a 371 of PCT/GB94/00010, filed on Jan. 5, 1994.

This invention concerns compositions, processes for the preparation of such compositions, two-pack systems for preparing such compositions and uses of such compositions. More particularly the present invention concerns compositions comprising dilute aqueous solutions of lower aliphatic peracids and their use as disinfectant compositions.

The lower aliphatic peracids are effective wide-spectrum bactericides which have the particular advantage, in use, of leaving as residues only the corresponding lower aliphatic acids and therefore being particularly suitable for applications which require a non-environmentally-polluting disinfectant. While the lower aliphatic peracids in general are contemplated herein, for example those corresponding to carboxylic aliphatic acids containing 2 to 9 carbon atoms, peracetic acid is particularly envisaged since it is already a commercially important peracid for disinfectant purposes. Where the following description relates to peracetic acid it is to be understood that the other peracids may be read in substitution therefor provided that the technical context allows it.

Aqueous solutions of peracetic acid containing up to about 45% by weight of peracetic acid are commercially available. Such solutions may be produced by reacting appropriately concentrated hydrogen peroxide and acetic acid in an aqueous medium in the presence of an acid catalyst which is usually sulphuric acid or other strong mineral acid. The acid catalyst may be present in from about 0.1% to about 5% by weight of the reaction mixture.

Aqueous solutions of peracetic acid represent equilibrium mixtures of the reactants and the reaction products and, under relatively forcing reaction conditions, for example when using one or more of a substantial quantity of catalyst, an elevated reaction temperature and a concentrated reaction mixture, equilibrium may be substantially reached in a relatively short time. When using the strong acid catalyst in from 2% to 5% of the reaction mixture, a temperature of from 30° C. to 50° C. and a concentration of acid above about 20% by weight the reaction mixture may come to equilibrium within hours. For some applications, or where long storage is envisaged, it may not be desirable for there to be catalyst residues in a peracid product and particularly, for example, in dilute products intended for personal or domestic hygiene use. For many applications dilute solutions of peracetic acid, for example below 5% by weight but often below 2%, for example from 0.1% to 2% by weight, are required. Concentrations of peracetic acid above 0.5% by weight for example from 0.5% to 1% by weight, are particularly effective bactericidally in, for example, toilet cleansing applications. Such dilute peracetic acid solutions may be produced directly by reacting acetic acid and hydrogen peroxide in a suitably dilute reaction medium but equilibrium can take an extremely long time to reach, particularly at the more extreme dilutions envisaged. At peracid concentrations below 1% by weight, equilibrium may take a month or more to reach if the reaction is not acid catalysed or a week or more even if the reaction is acid catalysed. This entails a very heavy utilisation of plant and equipment on a large production scale.

If a concentrated equilibrium solution of peracetic acid is diluted with water, the equilibrium point of the system is

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progressively altered, as dilution progresses, in favour of the regeneration of the original reactants. The ageing time taken to attain the new equilibrium point, after dilution, is of a similar order to that required to produce such a dilute solution directly from suitable reactants. Such a diluted solution may be used directly, although it is not at equilibrium and is therefore of variable composition in storage. Such non-equilibrium diluted solutions also have a composition dictated by the equilibrium point applying at the original concentration, which may not be desired in some applications.

In 1955 Greenspan et al. (Proc. 42nd Ann. Mtg. Chem. Spec. Man. Ass. December 1955), disclosed that stable dilute peracetic acid solutions can be prepared by the use of peracid stabilisers in conjunction with proper adjustment of the relative concentrations of the components of the dilute peracid solution, that is to say that, if the prepared dilute solution is not fully at equilibrium, adjustment of the balance of the components can achieve stability. The solutions in question may be prepared by dilution of commercial, e.g. fully equilibrated peracetic acid which has been produced by the use of small amounts of a mineral acid catalyst.

U.S. Pat. No. 4,297,298 describes the production of an aqueous solution of a lower aliphatic peracid by preparing in a first process step a concentrated solution of the peracid from the corresponding carboxylic acid or anhydride and concentrated hydrogen peroxide in the presence of a small quantity of a strong acid catalyst and diluting the solution with a solution containing at least one of the reagents from the first process step so as to bring the concentration of the aliphatic peracid to the rated concentration of the mixture the concentration of the diluent reagent or reagents being chosen "so that once dilution has been brought about, the system is no longer at equilibrium, but tends to move in the direction of forming further aliphatic peracid at a very slow rate." The process specifically described in U.S. Pat. No. 4,297,298 produces a non-equilibrium composition which contains an extremely high concentration of hydrogen peroxide, e.g. from 28% to 46%. Such a concentration on contact with the user would cause skin bleaching and pain.

U.S. Pat. No. 4,743,447 describes the production of solutions having a hydrogen peroxide base for disinfecting contact lenses, the solution having from 0.005% to 0.1% by weight of peracetic acid, 1% to 8% by weight of hydrogen peroxide and sufficient acetic acid for the system to reach equilibrium. Such a solution may be prepared by direct reaction using a very dilute reaction mixture with lengthy equilibration or from a stable commercial solution having a "weak concentration" of peracetic acid to which the other constituents of the composition are added. This teaching does not therefore avoid the separate initial step of producing a stable weak solution of peracetic acid from which to produce in turn the final product.

EP-A-0357238 (Steris Corp) discloses an anti-microbial composition comprising a strong oxidant, a copper and brass corrosion inhibitor, a buffering agent, at least one anti-corrosive agent which exhibits corrosion inhibition in at least aluminium, carbon steel and stainless steel, and a wetting agent. The corrosion inhibitors specifically disclosed for brass and aluminium comprise triazoles and molybdates, which are known to have unfavourable toxicity, and which therefore renders undesirable their use in a medical environment.

In certain cases, it is desirable for the peracetic acid composition employed as a disinfectant composition to be produced by dilution of a more concentrated peracetic acid solution with a second solution which can comprise com-

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ponents which may confer beneficial properties on the peracetic acid composition, such as corrosion inhibitors. In the absence of any counter measures, or even despite them, it is possible that the second solution can become contaminated with micro-organisms, for example, moulds and yeasts, during storage prior to mixing with the peracetic acid solution. Control of this is therefore desirable, but many of the compounds commonly recommended for such control are either incompatible with peracetic acid, or can be undesirable for medical use because of their toxicity.

It is an object of the present invention to provide a disinfectant composition, based on a dilute solution of peracid, which may be used on medical equipment comprising metal components to be disinfected.

It is a further object of certain embodiments of the present invention to provide a solution suitable for diluting peracetic acid to produce a composition which may be used on medical equipment comprising metal components, such solution having improved resistance to contamination by micro-organisms.

In accordance with the present invention there is provided a process for the preparation of an aqueous disinfectant composition characterised in that the process comprises mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising hydrogen peroxide, a corrosion inhibitor and a hydrogen peroxide stabilizer and/or peracid stabilizer.

In another aspect, the present invention provides a disinfectant composition obtainable by a process comprising mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising hydrogen peroxide, a corrosion inhibitor and a hydrogen peroxide stabilizer and/or peracid stabilizer. It is to be understood that the peracid composition of the present invention is not in equilibrium and comprises a relatively higher concentration of stabilizer(s) than a skilled person would expect to find in a composition which is in equilibrium and comprises a similar concentration of peracid.

In yet another aspect, the present invention provides a two-pack system for the preparation of a disinfectant composition, characterised in that one pack comprises a first aqueous solution comprising a lower aliphatic peracid, and the other pack comprises a second aqueous solution comprising hydrogen peroxide, a corrosion inhibitor and a hydrogen peroxide stabilizer and/or peracid stabilizer.

The first aqueous solution preferably comprises a lower aliphatic peracid, such as peracetic acid, in an amount of from 2% to 10%, more preferably from 3% to 7%, by weight of the solution. The first aqueous solution may additionally comprise stabilizer(s) for the hydrogen peroxide and/or the peracid in the equilibrium solution, each relevant stabilizer being present in a preferred amount of from 20 to 10,000 ppm. Preferably both the peroxide and peracid are stabilized in the solution, giving a preferred combined stabilizer concentration of from 3000 to 6000 ppm. A suitable peracid stabilizer is dipicolinic acid and suitable peroxide stabilizers include phosphonic acids and salts thereof, e.g. the products sold by Monsanto under the trade mark "Dequest" such as hydroxyethylidenedimethylene phosphonate, diethylenetriaminepentamethylene phosphonate and ethylenediaminetetra-methylene phosphonate and those stabilizers claimed in European patent application 0426949, especially cyclohexane-1,2-diaminetetra-methylene phosphonic acid and salts thereof (CDTMP). It should be understood that the first solution is usually an equilibrium mixture of the relevant reactants and reaction products, as generally described in the paragraph bridging page 1 and page 2 above, and that

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the above specified amount of peracid indicates the amount of peracid per se in the solution. A preferred process for the preparation of dilute solutions of lower aliphatic peracids useful in the present invention is disclosed in PCT Patent Application No. WO 91/13058.

The hydrogen peroxide present in the second aqueous solution is preferably present as a dilute solution. In many embodiments the concentration of hydrogen peroxide present in the second aqueous solution is unlikely to be greater than about 5% w/w. Preferably, the concentration of hydrogen peroxide is from about 0.025% w/w to about 1% w/w, most preferably from about 0.05% w/w to about 0.5% w/w and in some embodiments from 0.05% w/w to 0.2% w/w. The function of the hydrogen peroxide in the second aqueous solution is to inhibit the growth of microbial contaminants in the solution.

The second aqueous solution preferably comprises from 0.1% to 5%, more preferably from 0.1% to 1%, by weight of the solution of a corrosion inhibitor. Preferably, the corrosion inhibitor is an alkali metal phosphate, most preferably a potassium phosphate. Dipotassium hydrogen orthophosphate ( $K_2HPO_4$ ) is the most preferred corrosion inhibitor.

The second aqueous solution preferably comprises from about 0.1% to about 2%, often 0.1% to 1%, more preferably up to 0.7% by weight of the solution of hydrogen peroxide stabilizer and/or peracid stabilizer. Preferably a hydrogen peroxide stabilizer is used. The preferred peroxide stabilizers are phosphonic acids and salts thereof, for example, those described hereinabove as suitable for the first aqueous solution. A suitable peracid stabilizer is dipicolinic acid.

In particularly preferred embodiments, the second aqueous solution comprises from 0.025% to 1% w/w hydrogen peroxide, from 0.1% to 0.7% w/w of CDTMP and from 0.1 to 1% w/w of  $K_2HPO_4$ .

According to certain preferred embodiments of the present invention, there is provided a two-pack system for the preparation of a disinfectant composition, characterised in that one pack comprises a first aqueous solution comprising 3% to 7% w/w peracetic acid, and the other pack comprises a second aqueous solution comprising from 0.025% to 1% w/w hydrogen peroxide, from 0.1% to 0.7% w/w CDTMP and from 0.1% to 1% w/w of dipotassium orthophosphate.

Mixing of the first and second solutions give a disinfectant composition immediately after mixing comprising at least about 0.05% and generally not greater than about 1% by weight peracid. In many embodiments, the mixture of the two solutions immediately after mixing comprises from about 0.1% to about 0.25% or from about 0.25% to about 0.5% by weight peracid. The mixture also desirably comprises from about 0.1% to about 5% corrosion inhibitor and from about 0.1% to about 1% peroxide stabilizer and/or peracid stabilizer. Such mixtures can often be obtained conveniently by selecting a volume ratio of the first solution to the second solution which is often at least 1:5 and not usually greater than about 1:50, preferably from about 1:10 to about 1:30, taking into account the concentration of the components in each solution.

One or both of the aqueous solutions may contain other components useful in disinfectant compositions, e.g. a triazole corrosion inhibitor and/or a wetting agent, though the presence of these components is not essential to obtain the advantages of the invention (indeed, such components may be slightly detrimental). One or both of the solutions may contain an indicator, such as, for example, methyl red, which undergoes a color change to indicate that the two solutions have been mixed together.

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It will be appreciated that the compositions provided by the process of the present invention are not in equilibrium and that in the natural course of events the peracid component of the composition will tend towards equilibrium. For example, the composition described in the paragraph immediately above this paragraph will begin to change within a relatively short period of time from mixing the first and second solutions together and that as time passes the peracid concentration in the solution will reduce as it tends towards equilibrium. Normal equilibrium could be expected to be reached after about two days, assuming the peracid and/or peroxide does not decompose in that period.

The compositions of the present invention are particularly suitable for use as medical disinfectants. Preferably, the compositions are used to disinfect medical equipment which has metal, e.g. aluminium, brass, copper and especially steel, components required to be disinfected. For example, the composition is particularly useful for disinfection of endoscopes. The present invention may have a further advantage over the prior art compositions of Steris. The selected components of the invention composition interact to protect metal components, especially steel components, with regard to localised corrosion, eg pitting, as well as, if not better than, if molybdate, triazole and/or wetting agent were present. This is most surprising in light of the disclosure on page 4, lines 7 to 9, of Steris.

The present invention has the advantage of providing a dilute composition comprising a relatively high concentration of peracid. Furthermore, the process of the present invention enables a relatively longer shelf life for the separate aqueous solution than would be achieved if the composition was supplied per se.

The invention will now be further described, without limitation, with reference to the following examples:

#### EXAMPLE 1

##### Preparation of Composition according to the Present Invention

A solution of 5% w/w peracetic acid, 20% w/w hydrogen peroxide, 8% w/w acetic acid was diluted 14 times with a solution containing 0.1% w/w hydrogen peroxide, 1% w/w CDTMP (as supplied, 14% active w/w), 0.8% dipotassium hydrogen orthophosphate and 10 ppm 0.01% methyl red solution to form a solution containing 3,500 ppm peracetic acid.

#### EXAMPLE 2

##### Microbial Challenge Tests

A solution comprising 0.1% w/w hydrogen peroxide, 1% w/w CDTMP (as supplied, 14% active w/w) and 0.8% dipotassium hydrogen orthophosphate was tested in the German Society for Hygiene and Microbiology *in vitro* tests (DGHM Standards for the Examination and Determination of chemical Disinfectant Processes, 1981. *In vitro* tests, Determination of the bacteriostatic and fungistatic efficiency). The test organisms used were bacteria *Staphylococcus aureus*, ATCC 6538, *Pseudomonas aeruginosa*, ATCC 15442 and fungus *Candida albicans* ATCC 10231. The results of the tests showed inhibition of both bacterial and fungal growth in the solution.

A further challenge test was carried out against a solution comprising 0.4% w/w CDTMP (as 100%) and 0.8% dipotassium hydrogen orthophosphate with 0.3% w/w hydrogen peroxide. As a control the same formulation but with no

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hydrogen peroxide was employed. 200 ml of the solutions were challenged with 0.1 ml cultures of bacteria *Staphylococcus aureus*, ATCC 6538 (cell count  $18 \times 10^6$  cfu/ml) and *Pseudomonas aeruginosa*, ATCC 15442 (cell count  $3.0 \times 10^7$  cfu/ml) and fungi *Candida albicans* ATCC 10231 (cell count  $1.2 \times 10^6$  cfu/ml) at the start of the test, and with *Aspergillus niger* IMI 149007 (cell count  $2.9 \times 10^7$  spores/ml) after 7 days. The samples were stored for 6 months in screw top jars at ambient temperature and regularly analysed for surviving cultures. Surviving cultures were enumerated by dilution of 1 ml samples of the solutions in quarter-strength Ringers solution followed by culture as follows. For *Staphylococcus aureus* and *Pseudomonas aeruginosa*, 24 hr @ 37° C. in Tryptone Soya Broth, for *Candida albicans*, 72 hr @ 37° C. in Tryptone Soya Broth, for *Aspergillus niger*, until spores develop (5-10 days) @ 30° C. in Malt Extract Agar. For the control solution (not according to the present invention, the number of surviving colonies was between  $1.3 \times 10^6$  and  $2.4 \times 10^7$  cfu/ml, with the number being  $4.7 \times 10^6$  cfu/ml after 6 months. For the solution according to the present invention, there were no surviving colonies, except for 24 hours after the addition of *Aspergillus niger*, when  $4 \times 10^3$  cfu/ml was observed. After a further 24 hours storage, however, there were no surviving colonies.

The results of the microbial challenge tests showed that the compositions according to the present invention gave good inhibition of microbial growth, and could give excellent resistance to microbial contamination over long term storage.

#### EXAMPLE 3

##### Chemical Stability Trials

4 samples of a solution suitable for use as a second aqueous solution in the present invention (Formulation 1) containing 0.3% w/w hydrogen peroxide, 0.14% w/w CDTMP (as 100%), 0.8% dipotassium hydrogen orthophosphate, 0.3% benzotriazole and 10 ppm 0.01% methyl red solution were prepared. A further 4 samples containing an additional 0.2% benzotriazole (Formulation 2) were also prepared. Samples were stored for 1 month at each of ambient (ca. 20° C.), 28° C., 32° C. and 40° C. and analysed for hydrogen peroxide content. The results of the analyses showed that for both solutions, there was no loss of hydrogen peroxide at any of the storage temperatures. The samples were also employed to produce compositions according to the present invention containing ca. 3,500 ppm peracetic acid by 14 times dilution of a solution of 5% w/w peracetic acid, 20% w/w hydrogen peroxide and 8% w/w acetic acid. The solutions according to the present invention were analysed for peracetic acid and hydrogen peroxide content, stored for 5 days and then re-analysed for peracetic acid and hydrogen peroxide. The results are given below, and show excellent chemical stability.

Sample	1st Day		5th Day	
	% H <sub>2</sub> O <sub>2</sub>	% BAA	% H <sub>2</sub> O <sub>2</sub>	% BAA
Formulation 1				
Initial	2.16	0.37	2.15	0.34
1 month @ 20°C				
Ambient	2.03	0.37	2.21	0.26
28° C	2.01	0.34	2.10	0.24

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-continued

Sample Time	1st Day		5th Day	
	% H <sub>2</sub> O <sub>2</sub>	% PAA	% H <sub>2</sub> O <sub>2</sub>	% PAA
32° C.	2.05	0.34	2.11	0.26
40° C.	2.04	0.40	2.10	0.30
Formulation 2				
Initial	1.98	0.35	1.99	0.23
1 month @ Temp:				
Ambient	2.06	0.39	2.08	0.25
28° C.	2.08	0.35	2.11	0.26
32° C.	2.12	0.29	2.11	0.28
40° C.	2.06	0.35	2.02	0.26

## EXAMPLE 4

## Corrosivity Test

A solution of 5% w/w peracetic acid, 20% w/w hydrogen peroxide, 8% w/w acetic acid is diluted 25 times with a solution containing 0.3% w/w hydrogen peroxide, 0.14% w/w CDTMP (as 100%, <25 ppm chloride), 0.8% dipotassium hydrogen orthophosphate and 10 ppm 0.01% methyl red solution to form a disinfectant solution containing 2,000 ppm peracetic acid. Duplicate coupons of mild steel and stainless steel 316 are immersed for 72 hours in samples of the disinfectant solution at room temperature (average 20° C.). The disinfectant solution is completely replaced daily with fresh solution. Examination of the coupons on completion of the trial shows only very slight localised corrosion of the coupons.

## I claim:

1. A process for the preparation of an aqueous disinfectant composition comprising mixing a first aqueous equilibrium solution comprising a lower aliphatic peracid with a second aqueous solution comprising hydrogen peroxide, a corrosion inhibitor, and a hydrogen peroxide stabilizer and/or peracid stabilizer, said hydrogen peroxide being present in said second aqueous solution in an amount of up to 5% by weight and sufficient to inhibit the growth of microbial contaminants in said second aqueous solution.

2. A two-pack system for the preparation of a disinfectant composition, one pack comprising a first aqueous equilibrium solution comprising a lower aliphatic peracid, and the other pack comprising a second aqueous solution comprising hydrogen peroxide, a corrosion inhibitor, and a hydrogen peroxide stabilizer and/or peracid stabilizer, said hydrogen peroxide being present in said second aqueous solution in an amount of up to 5% by weight and sufficient to inhibit the growth of microbial contaminants in said second aqueous solution.

3. A process as claimed in claim 1, wherein the first aqueous solution comprises a (C<sub>2</sub>-C<sub>6</sub>) aliphatic peracid in an amount of from 2% to 10% by weight of the solution.

4. A process as claimed in claim 3, wherein the aliphatic peracid is present in the first aqueous solution in an amount of from 3% to 7% by weight of the solution.

5. A process as claimed in claim 1 wherein the second aqueous solution comprises from 0.1% to 5% by weight of the solution of said corrosion inhibitor.

6. A process as claimed in claim 5, wherein the second aqueous solution comprises from 0.1% to 1% by weight of the solution of said corrosion inhibitor.

7. A process as claimed in claim 5 or 6, wherein the corrosion inhibitor comprises an alkali metal phosphate.

8. A process as claimed in claim 7, wherein the corrosion inhibitor comprises dipotassium hydrogen orthophosphate.

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9. A process as claimed in any one of claims 1, 3, 4, 5 or 6, wherein the second aqueous solution comprises from 0.1% to about 2% by weight of the solution of said hydrogen peroxide stabilizer and/or peracid stabilizer.

10. A process as claimed in claim 9, wherein the second aqueous solution comprises from 0.1% to 0.7% by weight of the solution of said hydrogen peroxide stabilizer and/or peracid stabilizer.

11. A process as claimed in claim 1, wherein only a hydrogen peroxide stabilizer is used.

12. A process as claimed in claim 1 or claim 11, wherein the stabilizer in the second solution comprises a phosphonic acid or salt thereof.

13. A process as claimed in claim 12, wherein the stabilizer comprises cyclohexane-1,2-diaminotetramethylphosphonic acid or salt thereof.

14. A process as claimed in claim 1, wherein the second solution comprises from about 0.025% w/w to about 1% w/w hydrogen peroxide.

15. A process as claimed in claim 1, wherein the second solution comprises from about 0.05% w/w to about 0.2% w/w hydrogen peroxide.

16. A process as claimed in claim 1, wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is about 1:5 to 1:30.

17. A process as claimed in claim 1, wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is about 1:10 to about 1:30.

18. A process as claimed in claim 1, wherein one or both of the first and second aqueous solutions comprises an indicator which undergoes a color change when the solutions are mixed together.

19. A process according to claim 1 or 4 wherein said aliphatic peracid comprises peracetic acid.

20. A two-pack system as claimed in claim 2, wherein the first aqueous solution comprises a (C<sub>2</sub>-C<sub>6</sub>) aliphatic peracid in an amount of from 2% to 10% by weight of the solution.

21. A two-pack system as claimed in claim 20, wherein the aliphatic peracid is present in the first solution in an amount of from 3% to 7% by weight of the solution.

22. A two-pack system as claimed in claim 2, wherein the second aqueous solution comprises from 0.1% to 5% by weight of the solution of said corrosion inhibitor.

23. A two-pack system as claimed in claim 22, wherein the second aqueous solution comprises from 0.1% to 1% by weight of the solution of said corrosion inhibitor.

24. A two-pack system as claimed in claim 22 or 23, wherein said corrosion inhibitor comprises an alkali metal phosphate.

25. A two-pack system as claimed in claim 24, wherein the corrosion inhibitor comprises dipotassium hydrogen orthophosphate.

26. A two-pack system as claimed in any one of claims 20, 21, 22 or 23, wherein the second aqueous solution comprises from 0.1% to about 2% by weight of the solution of said hydrogen peroxide stabilizer and/or peracid stabilizer.

27. A two-pack system as claimed in claim 26 wherein the second aqueous solution comprises from 0.1% to 0.7% by weight of the solution of said hydrogen peroxide stabilizer and/or peracid stabilizer.

28. A two-pack system as claimed in claim 2, wherein only a hydrogen peroxide stabilizer is used.

29. A two-pack system as claimed in claim 2 or claim 28, wherein the stabilizer in the second solution comprises a phosphonic acid or salt thereof.

30. A two-pack system as claimed in claim 29, wherein the stabilizer comprises cyclohexane-1,2-diaminotetramethylphosphonic acid or salt thereof.



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31. A two-pack system as claimed in claim 2, wherein the second solution comprises from about 0.025% w/w to about 1% w/w hydrogen peroxide.

32. A two-pack system as claimed in claim 2, wherein the second solution comprises from about 0.05% w/w to about 0.2% w/w hydrogen peroxide.

33. A two-pack system as claimed in claim 2, wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is about 1:5 to 1:50.

34. A two-pack system as claimed in claim 2, wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is about 1:10 to about 1:30.

35. A two-pack system as claimed in claim 2, wherein said one pack comprises a first aqueous solution comprising 3% to 7% w/w peracetic acid, and the other pack comprises a second aqueous solution comprising from 0.025% to 1% w/w hydrogen peroxide, from 0.1% to 0.7% w/w CDTMP and from 0.1% to 1% w/w of dipotassium orthophosphate.

36. A two-pack system as claimed in claim 2, wherein one or both of the first and second aqueous solutions comprises an indicator which undergoes a color change when the solutions are mixed together.

37. A two-pack system as claimed in claim 2 or claim 20, wherein said aliphatic peracid comprises peracetic acid.

38. In a method of disinfecting a surface which comprises contacting a surface with an aqueous disinfectant solution

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comprising a lower aliphatic peracid, the improvement wherein the aqueous disinfectant solution is prepared by mixing a first aqueous equilibrium solution comprising a lower aliphatic peracid with a second aqueous solution comprising hydrogen peroxide, a corrosion inhibitor, and a hydrogen peroxide stabilizer and/or peracid stabilizer, said hydrogen peroxide being present in said second aqueous solution in an amount of up to 5% by weight and sufficient to inhibit the growth of microbial contaminants in said second aqueous solution.

39. An improved method according to claim 38, wherein said first and second aqueous solutions are provided in a two-pack system, one pack comprising said first aqueous equilibrium solution and the other pack comprising said second aqueous solution.

40. An improved method according to claim 38 or 39, wherein said surface comprises metal.

41. An improved method according to claim 40, wherein said metal comprises steel.

42. An improved method according to claim 38 or 39, wherein said surface comprises a metal surface of a medical instrument.

43. A method according to claim 42, wherein said medical instrument comprises an endoscope.

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**United States Patent** [19]  
**Revell**[11] **Patent Number:** **5,489,706**  
[45] **Date of Patent:** **Feb. 6, 1996**[54] **STABILIZED PERACID SOLUTIONS**[75] **Inventor:** Christopher Revell, Great Sankey,  
United Kingdom[73] **Assignee:** Solvay Interlox Limited, Warrington,  
United Kingdom[21] **Appl. No.:** 244,026[22] **PCT Filed:** Nov. 11, 1992[86] **PCT No.:** PCT/GB92/02087

§ 371 Date: May 13, 1994

§ 102(e) Date: May 13, 1994

[87] **PCT Pub. No.:** WO93/10088**PCT Pub. Date:** May 27, 1993[30] **Foreign Application Priority Data**

Nov. 14, 1991 [GB] United Kingdom 9124160

[51] **Int. CL<sup>6</sup>** C07C 179/133[52] **U.S. Cl.** 562/3; 562/2[58] **Field of Search** 562/2, 3[56] **References Cited****U.S. PATENT DOCUMENTS**

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**FOREIGN PATENT DOCUMENTS**

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*Primary Examiner*—José G. Dees*Assistant Examiner*—Samuel Barts*Attorney, Agent, or Firm*—Larson and Taylor[57] **ABSTRACT**

Disclosed is a process for improving the storage stability of peracetic acid comprising adding an effective concentration of preferably 0.1–5 wt. % of an aliphatic alcohol ethoxylate wetting agent which has an EO number of greater than 4.

**19 Claims, No Drawings**

## STABILIZED PERACID SOLUTIONS

This application is a 371 of PCT/GB92/02087 filed Nov. 11, 1992.

The present invention relates to stabilised peracid solutions and their production.

Soluble peracids have a number of attractive properties, including oxidative and broad spectrum biocidal properties. As a consequence, they have been employed or proposed for use as oxidising agents in chemical synthesis reactions, as bleaching agents in the bleaching or cleansing of laundry and other substrates and as disinfectants or sterilisers for especially liquid media or solid surfaces.

One peracid which is widely available and suitable for the above-mentioned uses is peracetic acid which is usually produced in an aqueous solution by reaction between acetic acid and hydrogen peroxide, optionally in the presence of a catalyst such as a strong acid, including sulphuric, phosphoric and/or phosphonic acids. In a number of commercially available peracetic acid-containing compositions, the peracetic acid is present in equilibrium with the two reactants from which it is produced and water. Although such compositions may be used immediately after their production, they are often stored for considerable periods during their distribution and/or by the end user. During storage there is a tendency for some decomposition of the peroxygen species to occur, thereby progressively impairing the effectiveness of the composition for its desired purpose or requiring the use of an increased amount to attain a desired concentration of active ingredient. Plainly, therefore, it is desirable to find ways of improving the stability of peracid compositions, by which is meant ways of ameliorating or inhibiting the rate at which the measured concentration of peroxygen compounds and particularly peracetic acid falls during storage. One method of apparently improving the peracid stability in peracid compositions is described by Henkel in British Patent Specification no 1 580 561, which comprises employing a higher concentration of hydrogen peroxide relative to the peracetic acid than an equilibrium concentration. Essentially the same concept is disclosed in European Patent 0 024 125 to L'Air Liquide, but augmented by simultaneously diluting the acid catalyst below a minimal level so as to retard the rate of re-equilibration of the composition. By using excess hydrogen peroxide inventors seek to balance peracetic acid generation arising from slow re-equilibration against its rate of decomposition. Disadvantageously, the use of a considerable excess of one of the reagents inevitably increases the cost of the final product.

An alternative method of improving the storage stability of peracetic acid solutions has been proposed in European Patent 0 147 207 to Albright & Wilson, namely the incorporation of certain C6-C18 alkyl substituted benzene sulphonate wetting agents. In the course of the present investigations, it has been found that certain other wetting agents can be even more effective than alkyl benzene sulphonates at stabilising peracetic acid solutions.

According to one aspect of the present invention, there is provided a process for improving the storage stability of peracetic acid in a solution containing a wetting agent characterised by introducing therein an effective concentration of an aliphatic alcohol ethoxylate wetting agent which has an EO number of greater than 4.

According to a second aspect of the invention, there are provided peracetic acid solutions having improved storage stability by introduction therein of an effective concentration of an aliphatic alcohol ethoxylate wetting agent which has an EO number of greater than 4.

Advantageously, it has been found that the introduction of the specified wetting agent improves the retention of the important constituent, namely the peracetic acid in solution relative to like compositions containing no wetting agent or an alkyl benzene sulphonate, though it may not improve the retention overall of peroxygen species in the solution during storage. In general, peracetic acid solutions are stored at ambient temperature, which can vary depending upon the locality and the time of year, but is often between about 0° and 35° C.

The amount of aliphatic alcohol ethoxylate employed in the processes and compositions of the present invention preferably is at least 0.1%, particularly at least 0.2% w/w and often at least 0.5% w/w of the peracetic acid solution. In many instances, its concentration in the solution is not greater than 5% w/w. In some embodiments a convenient range of concentrations combining the benefits of wetting and improved stability comprises from about 0.5 to about 2.5% w/w of the solution.

The aliphatic alcohol ethoxylates employed herein preferably have an EO number of at least 6, often up to about 25, and usually, on average, between about 8 and about 20. It will be recognised though that the EO number is an average and in individual molecules, the number of ethylene oxide units can be below, within or above the ranges stated above. The alcohol moiety preferably contains at least 6 carbons and often up to about 20 carbons on average. In many alcohol ethoxylates that are suitable for the present invention, the alcohol moiety contains on average a chain length of from 8 to 18 carbons. The alcohol moiety is often either a primary or a secondary alcohol. The alcohol ethoxylate can be introduced into the peracetic acid solution either during its manufacture or when it has been produced. Thus, in one variation, the alcohol ethoxylate is mixed with the reactants which form peracetic acid, viz the acetic acid and aqueous hydrogen peroxide solution, and the mixture is stored until a desired proportion of the reactants have been converted to peracetic acid. Conventional variants in the manufacturing process can be employed. Thus, optionally, the manufacture can employ a strong acid catalyst selected at the operator's discretion, often in the range of from 0.1 to 10% w/w and selected from sulphuric acid, phosphoric acid and organic phosphonic acids (e.g. hydroxyethylenediphosphonic acid) or a mixture of mineral acid and organic phosphonic acid. A suitable reaction temperature can be selected at the operator's discretion at from 5° to 95° C., and often from 15° to 60° C. Suitable reaction times, which can vary from minutes to days depending upon the reaction temperature and amount of catalyst present, can be calculated from published data, for example broadly as set out in a paper by Y. Sawaki and Y. Ogata published in December 1965 in the Bulletin of the Chemical Society of Japan vol 38 no 12, pp2103/6. Naturally, conventional and appropriate safety precautions are taken during manufacture that are commensurate with the selected reaction conditions, such as the use of an inert atmosphere at elevated reaction temperatures and adequate agitation of the mixture.

The concentration of peracetic acid in solution can be selected within a wide range, depending on its intended end use. Its concentration is usually at least 0.01% w/w often at least 0.1% w/w and normally up to about 40% w/w. In many instances, the peracetic acid concentration is from about 0.03% to about 15%; ready to use mixtures conveniently containing from 0.03 to 5% and dilutable concentrates often containing from about 10 to 15% w/w. The amounts of reactants can be selected to leave residual concentrations of them, viz hydrogen peroxide and acetic acid within wide

ranges, typically each having a selected residual in the range of from about 1 to about 40% w/w. The amounts of reagents to use can be calculated using data on the equilibrium point of the reaction. For many ready to use mixtures, the reactants concentrations are each often chosen in the range of up to about 15% w/w and for dilutable concentrates they are often chosen in the range of about 10 to about 30% w/w. It will be understood, of course, that where the compositions, as made, differ to a significant extent from the corresponding equilibrium mixture, there will be a tendency for further or re-equilibration to occur during subsequent storage.

The present invention is particularly applicable to peracetic acid compositions in which the peracetic acid, acetic acid, hydrogen peroxide and water therein are approximately in equilibrium.

For some purposes it is desirable to produce a peracetic acid solution which contains a wetting agent, but which also generates relatively little foaming on application. Advantageously, it has been found that the selection of alcohol ethoxylate according to the present invention can not only improve peracetic acid storage stability, but also enable a low-foaming wetting agent-containing composition to be formed.

The stabilised compositions of the present invention are especially suitable for spraying onto or otherwise contacting solid surfaces, for example equipment, apparatus, containers, pipework, work surfaces, sanitary ware and the like for the purposes of disinfecting or sanitising them, the wetting agent promoting contact between the solution and the surface.

Having described the invention in general terms, specific embodiments thereof will hereafter be described more explicitly, by way of example only.

#### Comparison 1 and 2 and Example 3

In each of these Comparisons and Example, a commercial equilibrated peracetic acid-containing composition was employed available from Interlox Chemicals Ltd. under their trade mark PROXITANE 0510, and containing nominally 5% w/w peracetic acid, 10% w/w acetic acid and 20% w/w hydrogen peroxide. In Comparison 2 and Example 3, 1.2 parts by weight of wetting agent were mixed into the peracetic acid composition at laboratory ambient temperature, about 22° C. The mixtures were stored at laboratory ambient temperature in translucent polyethylene storage bottles. The peracetic acid and total available oxygen (Avox) contents of each composition were determined at intervals during the storage, and the values obtained after 58 weeks storage are compared with their respective initial values and expressed below as a percentage of PAA and Avox retained, rounded to the nearest whole number. The total Avox content was measured using a standard ferric iron catalysed thio-sulphate/iodine titration, and the peracetic acid content was measured by subtracting from the total Avox content the hydrogen peroxide content obtained by ferroin-indicated titration with ceric sulphate solution.

TABLE 1

	Wetting agent	% Retained	
		PAA	Avox
Comparison 1	No wetting agent	86	90
Comparison 2	Alkylbenzenesulphonic acid (Alkyl = C12 approx)	85	95
Example 3	alcohol ethoxylate (Alkyl = C9, EO = 8)	88	91

From Table 1, it can be seen that the effect of employing the alkyl benzene sulphonic acid is to increase the overall Avox retention of the composition relative to the corresponding composition which did not contain wetting agent, but that the stability of the most active constituent, namely PAA, was actually slightly worse. On the other hand, when the alcohol ethoxylate was employed, the overall effect was to not only increase the stability slightly of the compositions when expressed as total Avox, but more importantly, a significant contribution to this improvement arose from the rather greater increase in stability of the most active constituent, PAA. This demonstrates the superiority of the alcohol ethoxylate for PAA stabilisation compared with an alkylbenzenesulphonic acid.

The compositions produced and tested in the foregoing Comparisons and Example were also tested to show their foaming and wetting properties.

The wetting trial was conducted by observing how long it took for a standard drop of sample to be absorbed by a piece of cotton (Brunchweiler).

The foaming trial was conducted by allowing the whole of a sample of 25 mls of composition to flow under gravity from a height of 25 cms from a wide-tipped burette into a measuring cylinder (100 mls) of diameter 28 mms placed underneath. The volume of foam generated initially and still present after 5 minutes is given in Table 2 below.

TABLE 2

	Wetting time (secs)	Volume of foam (mls)	
		Initially	5 minutes
Comparison 1	>300	0	0
Comparison 2	5	38	36
Example 3	5	32	17

From Table 2, it can be seen that one effect of incorporating the wetting agent is that the ability of the composition to wet a surface is markedly improved, and that when the alcohol ethoxylate is employed the extent of foam generated is detectably less than if an alkylbenzenesulphonic acid is employed, and the foam breaks down more quickly.

#### Comparisons 4 and 5 and Examples 6 to 8

In each of these Comparisons and Examples a solution was employed comprising peracetic acid, acetic acid and 6% hydrogen peroxide. In Comparison 5 and Examples 6 to 8, 2% of commercially available alcohol ethoxylates specified in Table 3 are mixed in at ambient temperature, about 22° C., and stored in polyethylene sample bottles.

The peracetic acid, hydrogen peroxide and total Avox contents of the compositions were measured at the start of the storage period and at regular intervals thereafter. The results after 8 months storage are also included in Table 3.

TABLE 3

	Wetting Agent		
	EO number	% Retained	
	Alkyl chain	PAA	Avox
Comparison 4	No wetting agents	82	100
Comparison 5	4 C12	80	100
Example 6	6.5 C9	85	100
Example 7	8 C9-11	89	100
Example 8	11 C13/15	92	100

From Table 3, it can be seen that although the total Avox retention was the same for all the compositions tested, there was a very significant change in the proportion of peracetic acid retained. When the EO number was only 4, as in comparison 5, the proportion retained was no better than when no wetting agent was present, but as the EO number increased, the proportion of peracetic acid which was retained increased.

#### Comparisons 9 and 10 and Examples 11 to 14

In these Comparisons and Examples non-equilibrium solutions containing approximately 300 ppm peracetic acid were obtained by diluting the commercially available peracetic acid composition of Comparison 1, PROXITANE 0510, with demineralised water. In comparison 10 and Examples 13 and 14, the composition was doped with 0.5% w/w sulphuric acid as re-equilibrium catalyst, and in Examples 11 to 14, the composition was mixed with a commercially available alcohol ethoxylate having an EO number of 7 and a 67%/33% mixture of C13 and C15 carbon chain lengths in the alcohol moiety. The compositions were stored in polyethylene bottles at ambient temperature, about 22° C., and the peracetic acid content measured periodically by a direct method thiosulphate/iodine titration at below -10° C. in ethane-1,2-diol. The results after 29 hours are listed in Table 4.

TABLE 4

	% Wetting Agent	% H <sub>2</sub> SO <sub>4</sub>	% PAA
Comparison 9	None		70
Comparison 10	None	0.5	56
Example 11	0.2	None	80
Example 12	1.0	None	100
Example 13	0.2	0.5	60
Example 14	1.0	0.5	100

From Table 4, it can be seen that the presence of the alcohol ethoxylate increased the proportion of peracetic acid retained in the composition, and that the effect was greater at the higher concentration of the wetting agent. This shows that the useful life of diluted non-equilibrium peracetic acid compositions can be extended by incorporating the selected alcohol ethoxylates according to the present invention.

I claim:

1. A process for improving the storage stability of peracetic acid solution, said process comprising introducing into said solution an aliphatic alcohol ethoxylate wetting agent which has an EO number of greater than 4 in an amount of at least 0.1% by weight and sufficient to improve the storage stability of the peracetic acid in the solution.
2. A process according to claim 1, wherein from 0.1 to 5% w/w of aliphatic alcohol ethoxylate is employed.
3. A process according to claim 2, wherein from 0.5 to 2.5% w/w of aliphatic alcohol ethoxylate is employed.
4. A process according to claim 1, wherein the aliphatic alcohol ethoxylate has an EO number of at least 6.
5. A process according to claim 4, wherein the aliphatic alcohol ethoxylate has an EO number of from 8 to about 20.
6. A process according to claim 1, wherein the alcohol moiety in the aliphatic alcohol ethoxylate contains at least 6 carbons.
7. A process according to claim 6, wherein the alcohol moiety in the aliphatic alcohol ethoxylate contains from 8 to 18 carbons.
8. A process according to claim 1, wherein the aliphatic alcohol ethoxylate is introduced into the mixture of reactants during the manufacture of the peracetic acid solution.
9. A process for improving the storage stability of peracetic acid solution, said process comprising introducing into said solution, from 0.5 to 2.5% w/w of an aliphatic alcohol ethoxylate wetting agent which has an EO number of from 8 to 20.
10. A process according to claim 1 or claim 9, wherein the solution to be stabilised contains from about 0.03 to about 15% w/w peracetic acid.
11. A peracetic acid solution having improved storage stability comprising an aliphatic alcohol ethoxylate wetting agent which has an EO number of greater than 4 in an amount of at least 0.1% by weight sufficient to improve the storage stability of the peracetic acid in the solution.
12. A solution according to claim 11, containing from 0.1 to 5% w/w of aliphatic alcohol ethoxylate.
13. A solution according to claim 12, containing from 0.5 to 2.5% w/w of aliphatic alcohol ethoxylate.
14. A solution according to claim 11, wherein the aliphatic alcohol ethoxylate has an EO number of at least 6.
15. A solution according to claim 14, wherein the aliphatic alcohol ethoxylate has an EO number of from about 8 to about 20.
16. A solution according to claim 11, wherein the alcohol moiety in the aliphatic alcohol ethoxylate contains at least 6 carbons.
17. A solution according to claim 16, wherein the alcohol moiety in the aliphatic alcohol ethoxylate contains from 8 to 18 carbons.
18. A peracetic acid solution having improved storage stability comprising from 0.5 to 2.5% w/w of an aliphatic alcohol ethoxylate wetting agent which has an EO number of from 8 to 20.
19. A solution according to claim 11 or 18, wherein the solution to be stabilised contains from about 0.03 to about 15% w/w peracetic acid.

\* \* \* \* \*

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US005545343A

# United States Patent [19]

Brougham et al.

[11] Patent Number: 5,545,343

[45] Date of Patent: Aug. 13, 1996

[54] PERACID COMPOSITIONS FOR MEDICAL DISINFECTION

[75] Inventors: Paul Brougham, Rainhill; Robert A. Simms, Woolston, both of United Kingdom

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[21] Appl. No.: 211,659

[22] PCT Filed: Oct. 8, 1992

[86] PCT No.: PCT/GB92/01830

§ 371 Date: Jun. 21, 1994

§ 102(e) Date: Jun. 21, 1994

[87] PCT Pub. No.: WO93/07909

PCT Pub. Date: Apr. 29, 1993

[30] Foreign Application Priority Data

Oct. 17, 1991 [GB] United Kingdom ..... 9122048

[51] Int. CL<sup>6</sup> ..... A01N 59/00

[52] U.S. CL. .... 514/557; 252/387; 252/389.2; 252/186.26; 422/28; 510/372

[58] Field of Search ..... 422/28, 32, 37; 562/3, 4, 6; 252/142, 95, 97, 173, 387, 389.2, 357

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Primary Examiner—Robert J. Warden

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Attorney, Agent, or Firm—Larson and Taylor

## [57] ABSTRACT

A multi-component product for providing, on mixing of the components, a disinfectant composition. A first component of the product comprises an aqueous solution of a lower aliphatic peracid and a second component comprises an aqueous solution containing a corrosion inhibitor and either a hydrogen peroxide stabilizer, a peracid stabilizer, or both.

30 Claims, No Drawings

## PERACID COMPOSITIONS FOR MEDICAL DISINFECTION

This invention concerns compositions, processes for the preparation of such compositions, two-pack systems for preparing such compositions and uses of such compositions. More particularly the present invention concerns compositions comprising dilute aqueous solutions of lower aliphatic peracids and their use as disinfectant compositions.

The lower aliphatic peracids are effective wide-spectrum bactericides which have the particular advantage, in use, of leaving as residues only the corresponding lower aliphatic acids and therefore being particularly suitable for applications which require a non-environmentally-polluting disinfectant. While the lower aliphatic peracids in general are contemplated herein, for example those corresponding to carboxylic aliphatic acids containing 2 to 9 carbon atoms, peracetic acid is particularly envisaged since it is already a commercially important peracid for disinfectant purposes. Where the following description relates to peracetic acid it is to be understood that the other peracids may be read in substitution therefor provided that the technical context allows it.

Aqueous solutions of peracetic acid containing up to about 45 % by weight of peracetic acid are commercially available. Such solutions may be produced by reacting appropriately concentrated hydrogen peroxide and acetic acid in an aqueous medium in the presence of an acid catalyst which is usually sulphuric acid or other strong mineral acid. The acid catalyst may be present in from about 0.1% to about 5% by weight of the reaction mixture.

Aqueous solutions of peracetic acid represent equilibrium mixtures of the reactants and the reaction products and, under relatively forcing reaction conditions, for example when using one or more of a substantial quantity of catalyst, an elevated reaction temperature and a concentrated reaction mixture, equilibrium may be substantially reached in a relatively short time. When using the strong acid catalyst in from 2% to 5% of the reaction mixture, a temperature of from 30° C. to 50° C. and a concentration of acid above about 20% by weight the reaction mixture may come to equilibrium within hours. For some applications, or where long storage is envisaged, it may not be desirable for there to be catalyst residues in a peracid product particularly, for example, dilute products intended for personal or domestic hygiene use. For many applications dilute solutions of peracetic acid, for example below 5% by weight but often below 2%, for example from 0.1% to 2% by weight, are required. Concentrations of peracetic acid above 0.5% by weight for example from 0.5% to 1% by weight, are particularly effective bactericidally in, for example, toilet cleansing applications. Such dilute peracetic acid solutions may be produced directly by reacting acetic acid and hydrogen peroxide in a suitably dilute reaction medium but equilibrium can take an extremely long time to reach, particularly at the more extreme dilutions envisaged. At peracid concentrations below 1% by weight equilibrium may take a month or more to reach if the reaction is not acid catalyzed or a week or more even if the reaction is acid catalyzed. This entails a very heavy utilization of plant and equipment on a large production scale.

If a concentrated equilibrium solution of peracetic acid is diluted with water the equilibrium point of the system is progressively altered, as dilution progresses, in favour of the regeneration of the original reactants. The ageing time taken to attain the new equilibrium point, after dilution, is of a similar order to that required to produce such a dilute

solution directly from suitable reactants. Such a diluted solution may be used directly although it is not at equilibrium and is therefore of variable composition in storage. Such non-equilibrium diluted solutions also have a composition dictated by the equilibrium point applying at the original concentration, which may not be desired in some applications. In 1955 Greenspan et al. (Proc. 42nd Ann. Mtg. Chem. Spec. Man. Ass. Dec. 1955), disclosed that stable dilute peracetic acid solutions can be prepared by the use of peracid stabilizers in conjunction with proper adjustment of the relative concentrations of the components of the dilute peracid solution, that is to say that, if the prepared dilute solution is not fully at equilibrium, adjustment of the balance of the components can achieve stability. The solutions in question may be prepared by dilution of commercial, e.g. fully equilibrated peracetic acid which has been produced by the use of small amounts of a mineral acid catalyst.

U.S. Pat. No. 4,297,298 describes the production of an aqueous solution of a lower aliphatic peracid by preparing in a first process step a concentrated solution of the peracid from the corresponding carboxylic acid or anhydride and concentrated hydrogen peroxide in the presence of a small quantity of a strong acid catalyst and diluting the solution with a solution containing at least one of the reagents from the first process step so as to bring the concentration of the aliphatic peracid to the rated concentration of the mixture the concentration of the diluent reagent or reagents being chosen "so that once dilution has been brought about, the system is no longer at equilibrium, but tends to move in the direction of forming further aliphatic peracid at a very slow rate." The process specifically described in U.S. Pat. No. 4,297,298 produces a non-equilibrium composition which contains an extremely high concentration of hydrogen peroxide, e.g. from 28% to 46%. Such a concentration on contact with the user would cause skin bleaching and pain.

U.S. Pat. No. 4,743,447 describes the production of solutions having a hydrogen peroxide base for disinfecting contact lenses, the solution having from 0.005% to 0.1% by weight of peracetic acid, 1% to 8% by weight of hydrogen peroxide and sufficient acetic acid for the system to reach equilibrium. Such a solution may be prepared by direct reaction using a very dilute reaction mixture with lengthy equilibration or from a stable commercial solution having a "weak concentration" of peracetic acid to which the other constituents of the composition are added. This teaching does not therefore avoid the separate initial step of producing a stable weak solution of peracetic acid from which to produce in turn the final product.

EP-A-0357238 (Steris Corp) discloses an anti-microbial composition comprising a strong oxidant, a copper and brass corrosion inhibitor, a buffering agent, at least one anti-corrosive agent which exhibits corrosion inhibition in at least aluminium, carbon steel and stainless steel, and a wetting agent. The corrosion inhibitors specifically disclosed for brass and aluminium comprise triazoles and molybdates, which are known to have unfavourable toxicity, and which therefore renders undesirable their use in a medical environment.

It is an object of the present invention to provide a disinfectant composition, based on a dilute solution of peracid, which may be used on medical equipment comprising metal components to be disinfected.

In accordance with the present invention there is provided a process for the preparation of an aqueous disinfectant composition characterized in that the process comprises mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising a corrosion inhibitor and a hydrogen peroxide stabilizer and/or peracid stabilizer.

In another aspect, the present invention provides a disinfectant composition obtainable by a process comprising mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising a corrosion inhibitor and a hydrogen peroxide stabilizer and/or peracid stabilizer. It is to be understood that the peracid composition of the present invention is not in equilibrium and comprises a relatively higher concentration of stabilizer(s) than a skilled person would expect to find in a composition which is in equilibrium and comprises a similar concentration of peracid.

In yet another aspect, the present invention provides a two-pack system for the preparation of a disinfectant composition, characterised in that one pack comprises a first aqueous solution comprising a lower aliphatic peracid, and the other pack comprises a second aqueous solution comprising a corrosion inhibitor and a hydrogen peroxide stabilizer and/or peracid stabilizer.

The first aqueous solution preferably comprises a lower aliphatic peracid, such as peracetic acid, in an amount of from 2% to 10%, more preferably from 3% to 7%, by weight of the solution. The first aqueous solution may additionally comprise stabilizer(s) for the hydrogen peroxide and/or the peracid in the equilibrium solution, each relevant stabilizer being present in a preferred amount of from 20 to 10,000 ppm. Preferably both the peroxide and peracid are stabilized in the solution, giving a preferred combined stabilizer concentration of from 3000 to 6000 ppm. A suitable peracid stabilizer is dipicolinic acid and suitable peroxide stabilizers include phosphonic acids and salts thereof, e.g. the products sold by Monsanto under the trade mark "DEQUEST" such as hydroxyethylidenediphosphonate, diethylenetriamine-pentamethylene phosphonate and ethylenediaminetetramethylene phosphonate and those stabilizers claimed in European patent application 0426949, especially cyclohexane-1, 2-diaminotetramethylenephosphonic acid and salts thereof (CDTMP). It should be understood that the first solution is usually an equilibrium mixture of the relevant reactants and reaction products, as generally described in the paragraph bridging page 1 and page 2 above, and that the above specified amount of peracid indicates the amount of peracid present in the solution. A preferred process for the preparation of dilute solutions of lower aliphatic peracids useful in the present invention is disclosed in PCT Patent Application No. WO 91/13058.

The second aqueous solution preferably comprises from 0.1% to 5%, more preferably from 0.1% to 1%, by weight of the solution of a corrosion inhibitor. Preferably, the corrosion inhibitor is an alkali metal phosphate, most preferably a potassium phosphate. Dipotassium hydrogen orthophosphate ( $K_2HPO_4$ ) is the most preferred corrosion inhibitor.

The second aqueous solution preferably comprises from 0.1% to 2%, often 0.1% to 1%, more preferably from 0.2% to 0.7% or 0.7% to 1%, by weight of the solution of hydrogen peroxide stabilizer and/or peracid stabilizer, such as about 0.5% or about 1% stabilizer. Preferably a hydrogen peroxide stabilizer is used. The preferred peroxide stabilizers are phosphonic acids and salts thereof, for example, those described hereinabove as suitable for the first aqueous solution. A suitable peracid stabilizer is dipicolinic acid.

Mixing of the first and second solutions give a disinfectant composition immediately after mixing comprising at least 0.05% and generally not greater than 1% by weight peracid. In many embodiments, the mixture of the two solutions immediately after mixing comprises from 0.1% to 0.25% or from 0.25% to 0.5% by weight peracid. The

mixture also desirably comprises from 0.1% to 5% corrosion inhibitor and from 0.1% to 1% peroxide stabilizer and/or peracid stabilizer. Such mixtures can often be obtained conveniently by selecting a volume ratio of the first solution to the second solution which is often at least 1:5 and not usually greater than 1:50, preferably from 1:10 to 1:30, taking into account the concentration of the components in each solution.

One or both of the aqueous solutions may contain other components useful in disinfectant compositions, e.g. a triazole corrosion inhibitor and/or a wetting agent, though the presence of these components is not essential to obtain the advantages of the invention (indeed, such components may be slightly detrimental). One or both of the solutions may contain an indicator which undergoes a colour change to indicate that the two solutions have been mixed together.

It will be appreciated that the compositions provided by the process of the present invention are not in equilibrium and that in the natural course of events the peracid component of the composition will tend towards equilibrium. For example, the composition described in the paragraph immediately above this paragraph will begin to change within a relatively short period of time from mixing the first and second solutions together and that as time passes the peracid concentration in the solution will reduce as it tends towards equilibrium. Normal equilibrium could be expected to be reached after about two days, assuming the peracid and/or peroxide does not decompose in that period.

The compositions of the present invention are particularly suitable for use as medical disinfectants. Preferably, the compositions are used to disinfect medical equipment which has metal, e.g. aluminium, brass, copper and especially steel, components required to be disinfected. For example, the composition is particularly useful for disinfection of endoscopes. The present invention may have a further advantage over the prior art compositions of Steris. The selected components of the invention composition interact to protect metal components, especially steel components, with regard to localized corrosion, e.g. pitting, as well as, if not better than, if molybdate, triazole and/or wetting agent were present. This is most surprising in light of the disclosure on page 4, lines 7 to 9, of Steris.

The present invention has the advantage of providing a dilute composition comprising a relatively high concentration of peracid. Furthermore, the process of the present invention enables a relatively longer shelf life for the separate aqueous solution than would be achieved if the composition was supplied per se.

The invention will now be further described, without limitation, with reference to the following examples:

#### EXAMPLE 1

Preparation of Composition according to the Present Invention

A two-pack system was prepared. One pack contained 250 ml of an aqueous peracetic acid, 5% (active) by weight, solution. The other pack contained 10 l of an aqueous solution comprising 0.6% by weight dipotassium hydrogen ortho phosphate and 0.5% by weight CDTMP. The two packs were then mixed together to form a composition of the present invention.

#### EXAMPLE 2

Preparation of Composition according to the Present Invention



A solution of 5% w/w peracetic acid, 20% w/w hydrogen peroxide, 8% w/w acetic acid was diluted 14 times with a solution containing 1% w/w CDTMP and 0.8% dipotassium hydrogen orthophosphate to form a solution containing 3,500 ppm peracetic acid.

### EXAMPLE 3 AND COMPARISON A

#### Corrosion Trials for Disinfectant Compositions

Duplicate coupons of mild steel and stainless steel 316 were immersed for 72 hours at room temperature (15°-25° C.) in disinfectant solutions. In Example 3, the disinfectant solution was prepared according to the method of Example 2 after a dilution by 25 times to produce a solution containing 2000 ppm peracetic acid. In Comparison A, the disinfectant solution was prepared according to the example given in the first table, page 6, lines 1 to 18 of European Patent Application No 0 357 238. The solutions were completely replaced daily with fresh solutions. Examination of the coupons with both the naked eye and an optical microscope on completion of the trial showed that for both of the metals in the composition according to the Steris Application, there was significant localized corrosion and pitting on the metal but for the metals in the disinfectant solution according to the present invention there was only very slight localised corrosion.

The significant reduction in localized corrosion achieved with compositions according to the present invention is surprising given the disclosure on page 4, lines 7 to 9 of the Steris Application, and is particularly advantageous because the results were achieved without the use of any toxic molybdate and triazole.

We claim:

1. A process for the preparation of an aqueous disinfectant composition comprising mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising a phosphate corrosion inhibitor and at least one hydrogen peroxide stabilizer selected from the group consisting of phosphonic acids and salts thereof.
2. A process as claimed in claim 1, wherein the first aqueous solution comprises a ( $C_2-C_9$ ) aliphatic peracid in an amount of from 2% to 10% by weight of the first aqueous solution.
3. A process as claimed in claim 1, wherein the first aqueous solution comprises a ( $C_2-C_9$ ) aliphatic peracid in an amount of from 3% to 7% by weight of the first aqueous solution.
4. A process as claimed in claim 2 or 3, wherein the aliphatic peracid comprises peracetic acid.
5. A process as claimed in claim 1, 2 or 3 wherein the second aqueous solution comprises from 0.1% to 5% by weight of the second aqueous solution of the phosphate corrosion inhibitor.
6. A process as claimed in claim 5, wherein the second aqueous solution comprises from 0.1% to 1% by weight of the second aqueous solution of the phosphate corrosion inhibitor.
7. A process as claimed in claim 5, wherein the phosphate corrosion inhibitor comprises an alkali metal phosphate.
8. A process as claimed in claim 6 wherein the phosphate corrosion inhibitor comprises dipotassium hydrogen orthophosphate.
9. A process as claimed in claim 1 wherein the second aqueous solution comprises from 0.1% to 2% by weight of the second aqueous solution of said at least one hydrogen peroxide stabilizer.
10. A process as claimed in claim 9 wherein the second

aqueous solution comprises from 0.2% to 1% by weight of the second aqueous solution of said at least one hydrogen peroxide stabilizer.

11. A process as claimed in claim 1 wherein said hydrogen peroxide stabilizer comprises cyclohexane-1, 2-diaminotetramethylenephosphonic acid or salt thereof.

12. A process as claimed in claim 1, 2, 3, 9 or 10, wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:5 to 1:50.

13. A process as claimed in claim 12 wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:10 to 1:30.

14. A process as claimed in claim 1, 2, 3, 9 or 10, wherein at least one of the first and second aqueous solutions comprises an indicator which undergoes a colour change when the solutions are mixed together.

15. A process according to any one of claims 1, 2, 3, 9 or 10, wherein said phosphate corrosion inhibitor comprises a steel corrosion inhibitor.

16. A multi-component product for providing, on mixing of the components, a disinfectant composition, said product comprising a first component which comprises a first aqueous solution comprising a lower aliphatic peracid, and a second component which comprises a second aqueous solution comprising a phosphate corrosion inhibitor and at least one hydrogen peroxide stabilizer selected from the group consisting of phosphonic acids and salts thereof.

17. A multi-component product as claimed in claim 16, wherein the first aqueous solution comprises a ( $C_2-C_9$ ) aliphatic peracid in an amount of from 2% to 10% by weight of the first aqueous solution.

18. A multi-component product as claimed in claim 16, wherein the first aqueous solution comprises a ( $C_2-C_9$ ) aliphatic peracid in an amount of from 3% to 7% by weight of the first aqueous solution.

19. A multi-component product as claimed in claim 17 or 18, wherein the aliphatic peracid comprises peracetic acid.

20. A multi-component product as claimed in claim 16, 17 or 18 wherein the second aqueous solution comprises from 0.1% to 5% by weight of the second aqueous solution of the phosphate corrosion inhibitor.

21. A multi-component product as claimed in claim 20, wherein the second aqueous solution comprises from 0.1% to 1% by weight of the second aqueous solution of the phosphate corrosion inhibitor.

22. A multi-component product as claimed in claim 20, wherein the phosphate corrosion inhibitor comprises an alkali metal phosphate.

23. A multi-component product as claimed in claim 21 wherein the phosphate corrosion inhibitor comprises dipotassium hydrogen orthophosphate.

24. A multi-component product as claimed in claim 16 wherein the second aqueous solution comprises from 0.1% to 2% by weight of the second aqueous solution of said at least one hydrogen peroxide stabilizer.

25. A multi-component product as claimed in claim 28 wherein the second aqueous solution comprises from 0.2% to 1% by weight of the second aqueous solution of said at least one hydrogen peroxide stabilizer.

26. A multi-component product as claimed in claim 16 wherein said hydrogen peroxide stabilizer comprises cyclohexane-1, 2-diaminotetramethylenephosphonic acid or salt thereof.

27. A multi-component product as claimed in claim 16, 17, 18, 24 or 25, wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:5 to 1:50.

28. A multi-component product as claimed in claim 27 wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:10 to 1:30.

29. A multi-component product as claimed in claim 16, 17, 18, 24 or 25, wherein at least one of the first and second

aqueous solutions comprises an indicator which undergoes a colour change when the solutions are mixed together.

30. A multi-component product according to any one of claims 16, 17, 18, 24 or 25, wherein said phosphate corrosion inhibitor comprises a steel corrosion inhibitor.

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US005545343A

**United States Patent** [19]

**Brougham et al.**

[11] **Patent Number:** **5,545,343**

[45] **Date of Patent:** **Aug. 13, 1996**

[54] **PERACID COMPOSITIONS FOR MEDICAL DISINFECTION**

[75] **Inventors:** Paul Brougham, Rainhill; Robert A. Simms, Woolston, both of United Kingdom

[73] **Assignee:** Solvay Interox Limited, Warrington, United Kingdom

[21] **Appl. No.:** 211,659

[22] **PCT Filed:** Oct. 8, 1992

[86] **PCT No.:** PCT/GB92/01830

§ 371 Date: Jun. 21, 1994

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[87] **PCT Pub. No.:** WO93/07909

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[30] **Foreign Application Priority Data**

Oct. 17, 1991 [GB] United Kingdom 9122048

[51] **Int. CL<sup>6</sup>** A01N 59/00

[52] **U.S. CL** 514/557; 252/387; 252/389.2; 252/186.26; 422/28; 510/372

[58] **Field of Search** 422/28, 32, 37; 562/3, 4, 6; 252/142, 95, 97, 173, 387, 389.2, 357

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*Assistant Examiner*—Hien Tran

*Attorney, Agent, or Firm*—Larson and Taylor

[57] **ABSTRACT**

A multi-component product for providing, on mixing of the components, a disinfectant composition. A first component of the product comprises an aqueous solution of a lower aliphatic peracid and a second component comprises an aqueous solution containing a corrosion inhibitor and either a hydrogen peroxide stabilizer, a peracid stabilizer, or both.

**30 Claims, No Drawings**

# PERACID COMPOSITIONS FOR MEDICAL DISINFECTION

This invention concerns compositions, processes for the preparation of such compositions, two-pack systems for preparing such compositions and uses of such compositions. More particularly the present invention concerns compositions comprising dilute aqueous solutions of lower aliphatic peracids and their use as disinfectant compositions.

The lower aliphatic peracids are effective wide-spectrum bactericides which have the particular advantage, in use, of leaving as residues only the corresponding lower aliphatic acids and therefore being particularly suitable for applications which require a non-environmentally-polluting disinfectant. While the lower aliphatic peracids in general are contemplated herein, for example those corresponding to carboxylic aliphatic acids containing 2 to 9 carbon atoms, peracetic acid is particularly envisaged since it is already a commercially important peracid for disinfectant purposes. Where the following description relates to peracetic acid it is to be understood that the other peracids may be read in substitution therefor provided that the technical context allows it.

Aqueous solutions of peracetic acid containing up to about 45 % by weight of peracetic acid are commercially available. Such solutions may be produced by reacting appropriately concentrated hydrogen peroxide and acetic acid in an aqueous medium in the presence of an acid catalyst which is usually sulphuric acid or other strong mineral acid. The acid catalyst may be present in from about 0.1% to about 5% by weight of the reaction mixture.

Aqueous solutions of peracetic acid represent equilibrium mixtures of the reactants and the reaction products and, under relatively forcing reaction conditions, for example when using one or more of a substantial quantity of catalyst, an elevated reaction temperature and a concentrated reaction mixture, equilibrium may be substantially reached in a relatively short time. When using the strong acid catalyst in from 2% to 5% of the reaction mixture, a temperature of from 30° C. to 50° C. and a concentration of acid above about 20% by weight the reaction mixture may come to equilibrium within hours. For some applications, or where long storage is envisaged, it may not be desirable for there to be catalyst residues in a peracid product particularly, for example, dilute products intended for personal or domestic hygiene use. For many applications dilute solutions of peracetic acid, for example below 5% by weight but often below 2%, for example from 0.1% to 2% by weight, are required. Concentrations of peracetic acid above 0.5% by weight for example from 0.5% to 1% by weight, are particularly effective bactericidally in, for example, toilet cleansing applications. Such dilute peracetic acid solutions may be produced directly by reacting acetic acid and hydrogen peroxide in a suitably dilute reaction medium but equilibrium can take an extremely long time to reach, particularly at the more extreme dilutions envisaged. At peracid concentrations below 1% by weight equilibrium may take a month or more to reach if the reaction is not acid catalyzed or a week or more even if the reaction is acid catalyzed. This entails a very heavy utilization of plant and equipment on a large production scale.

If a concentrated equilibrium solution of peracetic acid is diluted with water the equilibrium point of the system is progressively altered, as dilution progresses, in favour of the regeneration of the original reactants. The ageing time taken to attain the new equilibrium point, after dilution, is of a similar order to that required to produce such a dilute

solution directly from suitable reactants. Such a diluted solution may be used directly although it is not at equilibrium and is therefore of variable composition in storage. Such non-equilibrium diluted solutions also have a composition dictated by the equilibrium point applying at the original concentration, which may not be desired in some applications. In 1955 Greenspan et al. (Proc. 42nd Ann. Mtg. Chem. Spec. Man. Ass. Dec. 1955), disclosed that stable dilute peracetic acid solutions can be prepared by the use of peracid stabilizers in conjunction with proper adjustment of the relative concentrations of the components of the dilute peracid solution, that is to say that, if the prepared dilute solution is not fully at equilibrium, adjustment of the balance of the components can achieve stability. The solutions in question may be prepared by dilution of commercial, e.g. fully equilibrated peracetic acid which has been produced by the use of small amounts of a mineral acid catalyst.

U.S. Pat. No. 4,297,298 describes the production of an aqueous solution of a lower aliphatic peracid by preparing in a first process step a concentrated solution of the peracid from the corresponding carboxylic acid or anhydride and concentrated hydrogen peroxide in the presence of a small quantity of a strong acid catalyst and diluting the solution with a solution containing at least one of the reagents from the first process step so as to bring the concentration of the aliphatic peracid to the rated concentration of the mixture the concentration of the diluent reagent or reagents being chosen "so that once dilution has been brought about, the system is no longer at equilibrium, but tends to move in the direction of forming further aliphatic peracid at a very slow rate." The process specifically described in U.S. Pat. No. 4,297,298 produces a non-equilibrium composition which contains an extremely high concentration of hydrogen peroxide, e.g. from 28% to 46%. Such a concentration on contact with the user would cause skin bleaching and pain.

U.S. Pat. No. 4,743,447 describes the production of solutions having a hydrogen peroxide base for disinfecting contact lenses, the solution having from 0.005% to 0.1% by weight of peracetic acid, 1% to 8% by weight of hydrogen peroxide and sufficient acetic acid for the system to reach equilibrium. Such a solution may be prepared by direct reaction using a very dilute reaction mixture with lengthy equilibration or from a stable commercial solution having a "weak concentration" of peracetic acid to which the other constituents of the composition are added. This teaching does not therefore avoid the separate initial step of producing a stable weak solution of peracetic acid from which to produce in turn the final product.

EP-A-0357238 (Steris Corp) discloses an anti-microbial composition comprising a strong oxidant, a copper and brass corrosion inhibitor, a buffering agent, at least one anti-corrosive agent which exhibits corrosion inhibition in at least aluminium, carbon steel and stainless steel, and a wetting agent. The corrosion inhibitors specifically disclosed for brass and aluminium comprise triazoles and molybdates, which are known to have unfavourable toxicity, and which therefore renders undesirable their use in a medical environment.

It is an object of the present invention to provide a disinfectant composition, based on a dilute solution of peracid, which may be used on medical equipment comprising metal components to be disinfected.

In accordance with the present invention there is provided a process for the preparation of an aqueous disinfectant composition characterized in that the process comprises mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising a corrosion inhibitor and a hydrogen peroxide stabilizer and/or peracid stabilizer.

In another aspect, the present invention provides a disinfectant composition obtainable by a process comprising mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising a corrosion inhibitor and a hydrogen peroxide stabilizer and/or peracid stabilizer. It is to be understood that the peracid composition of the present invention is not in equilibrium and comprises a relatively higher concentration of stabilizer(s) than a skilled person would expect to find in a composition which is in equilibrium and comprises a similar concentration of peracid.

In yet another aspect, the present invention provides a two-pack system for the preparation of a disinfectant composition, characterised in that one pack comprises a first aqueous solution comprising a lower aliphatic peracid, and the other pack comprises a second aqueous solution comprising a corrosion inhibitor and a hydrogen peroxide stabilizer and/or peracid stabilizer.

The first aqueous solution preferably comprises a lower aliphatic peracid, such as peracetic acid, in an amount of from 2% to 10%, more preferably from 3% to 7%, by weight of the solution. The first aqueous solution may additionally comprise stabilizer(s) for the hydrogen peroxide and/or the peracid in the equilibrium solution, each relevant stabilizer being present in a preferred amount of from 20 to 10,000 ppm. Preferably both the peroxide and peracid are stabilized in the solution, giving a preferred combined stabilizer concentration of from 3000 to 6000 ppm. A suitable peracid stabilizer is dipicolinic acid and suitable peroxide stabilizers include phosphonic acids and salts thereof, e.g. the products sold by Monsanto under the trade mark "DEQUEST" such as hydroxyethylidenediphosphonate, diethylenetriamine-pentamethylene phosphonate and ethylenediaminetetramethylene phosphonate and those stabilizers claimed in European patent application 0426949, especially cyclohexane-1,2-diaminotetramethylenephosphonic acid and salts thereof (CDTMP). It should be understood that the first solution is usually an equilibrium mixture of the relevant reactants and reaction products, as generally described in the paragraph bridging page 1 and page 2 above, and that the above specified amount of peracid indicates the amount of peracid per se in the solution. A preferred process for the preparation of dilute solutions of lower aliphatic peracids useful in the present invention is disclosed in PCT Patent Application No. WO 91/13058.

The second aqueous solution preferably comprises from 0.1% to 5%, more preferably from 0.1% to 1%, by weight of the solution of a corrosion inhibitor. Preferably, the corrosion inhibitor is an alkali metal phosphate, most preferably a potassium phosphate. Dipotassium hydrogen orthophosphate ( $K_2HPO_4$ ) is the most preferred corrosion inhibitor.

The second aqueous solution preferably comprises from 0.1% to 2%, often 0.1% to 1%, more preferably from 0.2% to 0.7% or 0.7% to 1%, by weight of the solution of hydrogen peroxide stabilizer and/or peracid stabilizer, such as about 0.5% or about 1% stabilizer. Preferably a hydrogen peroxide stabilizer is used. The preferred peroxide stabilizers are phosphonic acids and salts thereof, for example, those described hereinabove as suitable for the first aqueous solution. A suitable peracid stabilizer is dipicolinic acid.

Mixing of the first and second solutions give a disinfectant composition immediately after mixing comprising at least 0.05% and generally not greater than 1% by weight peracid. In many embodiments, the mixture of the two solutions immediately after mixing comprises from 0.1% to 0.25% or from 0.25% to 0.5% by weight peracid. The

mixture also desirably comprises from 0.1% to 5% corrosion inhibitor and from 0.1% to 1% peroxide stabilizer and/or peracid stabilizer. Such mixtures can often be obtained conveniently by selecting a volume ratio of the first solution to the second solution which is often at least 1:5 and not usually greater than 1:50, preferably from 1:10 to 1:30, taking into account the concentration of the components in each solution.

One or both of the aqueous solutions may contain other components useful in disinfectant compositions, e.g. a triazole corrosion inhibitor and/or a wetting agent, though the presence of these components is not essential to obtain the advantages of the invention (indeed, such components may be slightly detrimental). One or both of the solutions may contain an indicator which undergoes a colour change to indicate that the two solutions have been mixed together.

It will be appreciated that the compositions provided by the process of the present invention are not in equilibrium and that in the natural course of events the peracid component of the composition will tend towards equilibrium. For example, the composition described in the paragraph immediately above this paragraph will begin to change within a relatively short period of time from mixing the first and second solutions together and that as time passes the peracid concentration in the solution will reduce as it tends towards equilibrium. Normal equilibrium could be expected to be reached after about two days, assuming the peracid and/or peroxide does not decompose in that period.

The compositions of the present invention are particularly suitable for use as medical disinfectants. Preferably, the compositions are used to disinfect medical equipment which has metal, e.g. aluminium, brass, copper and especially steel, components required to be disinfected. For example, the composition is particularly useful for disinfection of endoscopes. The present invention may have a further advantage over the prior art compositions of Steris. The selected components of the invention composition interact to protect metal components, especially steel components, with regard to localized corrosion, e.g. pitting, as well as, if not better than, if molybdate, triazole and/or wetting agent were present. This is most surprising in light of the disclosure on page 4, lines 7 to 9, of Steris.

The present invention has the advantage of providing a dilute composition comprising a relatively high concentration of peracid. Furthermore, the process of the present invention enables a relatively longer shelf life for the separate aqueous solution than would be achieved if the composition was supplied per se.

The invention will now be further described, without limitation, with reference to the following examples:

#### EXAMPLE 1

Preparation of Composition according to the Present Invention

A two-pack system was prepared. One pack contained 250 ml of an aqueous peracetic acid, 5% (active) by weight, solution. The other pack contained 10 l of an aqueous solution comprising 0.6% by weight dipotassium hydrogen ortho phosphate and 0.5% by weight CDTMP. The two packs were then mixed together to form a composition of the present invention.

#### EXAMPLE 2

Preparation of Composition according to the Present Invention

A solution of 5% w/w peracetic acid, 20% w/w hydrogen peroxide, 8% w/w acetic acid was diluted 14 times with a solution containing 1% w/w CDTMP and 0.8% dipotassium hydrogen orthophosphate to form a solution containing 3,500 ppm peracetic acid.

### EXAMPLE 3 AND COMPARISON A

#### Corrosion Trials for Disinfectant Compositions

Duplicate coupons of mild steel and stainless steel 316 were immersed for 72 hours at room temperature (15°–25° C.) in disinfectant solutions. In Example 3, the disinfectant solution was prepared according to the method of Example 2 after a dilution by 25 times to produce a solution containing 2000 ppm peracetic acid. In Comparison A, the disinfectant solution was prepared according to the example given in the first table, page 6, lines 1 to 18 of European Patent Application No 0 357 238. The solutions were completely replaced daily with fresh solutions. Examination of the coupons with both the naked eye and an optical microscope on completion of the trial showed that for both of the metals in the composition according to the Steris Application, there was significant localized corrosion and pitting on the metal but for the metals in the disinfectant solution according to the present invention there was only very slight localized corrosion.

The significant reduction in localized corrosion achieved with compositions according to the present invention is surprising given the disclosure on page 4, lines 7 to 9 of the Steris Application, and is particularly advantageous because the results were achieved without the use of any toxic molybdate and triazole.

We claim:

1. A process for the preparation of an aqueous disinfectant composition comprising mixing a first aqueous solution comprising a lower aliphatic peracid with a second aqueous solution comprising a phosphate corrosion inhibitor and at least one hydrogen peroxide stabilizer selected from the group consisting of phosphonic acids and salts thereof.

2. A process as claimed in claim 1, wherein the first aqueous solution comprises a (C<sub>2</sub>–C<sub>9</sub>) aliphatic peracid in an amount of from 2% to 10% by weight of the first aqueous solution.

3. A process as claimed in claim 1, wherein the first aqueous solution comprises a (C<sub>2</sub>–C<sub>9</sub>) aliphatic peracid in an amount of from 3% to 7% by weight of the first aqueous solution.

4. A process as claimed in claim 2 or 3, wherein the aliphatic peracid comprises peracetic acid.

5. A process as claimed in claim 1, 2 or 3 wherein the second aqueous solution comprises from 0.1% to 5% by weight of the second aqueous solution of the phosphate corrosion inhibitor.

6. A process as claimed in claim 5, wherein the second aqueous solution comprises from 0.1% to 1% by weight of the second aqueous solution of the phosphate corrosion inhibitor.

7. A process as claimed in claim 5, wherein the phosphate corrosion inhibitor comprises an alkali metal phosphate.

8. A process as claimed in claim 6 wherein the phosphate corrosion inhibitor comprises dipotassium hydrogen orthophosphate.

9. A process as claimed in claim 1 wherein the second aqueous solution comprises from 0.1% to 2% by weight of the second aqueous solution of said at least one hydrogen peroxide stabilizer.

10. A process as claimed in claim 9 wherein the second

aqueous solution comprises from 0.2% to 1% by weight of the second aqueous solution of said at least one hydrogen peroxide stabilizer.

11. A process as claimed in claim 1 wherein said hydrogen peroxide stabilizer comprises cyclohexane-1, 2-diaminotetramethylenephosphonic acid or salt thereof.

12. A process as claimed in claim 1, 2, 3, 9 or 10, wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:5 to 1:50.

13. A process as claimed in claim 12 wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:10 to 1:30.

14. A process as claimed in claim 1, 2, 3, 9 or 10, wherein at least one of the first and second aqueous solutions comprises an indicator which undergoes a colour change when the solutions are mixed together.

15. A process according to any one of claims 1, 2, 3, 9 or 10, wherein said phosphate corrosion inhibitor comprises a steel corrosion inhibitor.

16. A multi-component product for providing, on mixing of the components, a disinfectant composition, said product comprising a first component which comprises a first aqueous solution comprising a lower aliphatic peracid, and a second component which comprises a second aqueous solution comprising a phosphate corrosion inhibitor and at least one hydrogen peroxide stabilizer selected from the group consisting of phosphonic acids and salts thereof.

17. A multi-component product as claimed in claim 16, wherein the first aqueous solution comprises a (C<sub>2</sub>–C<sub>9</sub>) aliphatic peracid in an amount of from 2% to 10% by weight of the first aqueous solution.

18. A multi-component product as claimed in claim 16, wherein the first aqueous solution comprises a (C<sub>2</sub>–C<sub>9</sub>) aliphatic peracid in an amount of from 3% to 7% by weight of the first aqueous solution.

19. A multi-component product as claimed in claim 17 or 18, wherein the aliphatic peracid comprises peracetic acid.

20. A multi-component product as claimed in claim 16, 17 or 18 wherein the second aqueous solution comprises from 0.1% to 5% by weight of the second aqueous solution of the phosphate corrosion inhibitor.

21. A multi-component product as claimed in claim 20, wherein the second aqueous solution comprises from 0.1% to 1% by weight of the second aqueous solution of the phosphate corrosion inhibitor.

22. A multi-component product as claimed in claim 20, wherein the phosphate corrosion inhibitor comprises an alkali metal phosphate.

23. A multi-component product as claimed in claim 21 wherein the phosphate corrosion inhibitor comprises dipotassium hydrogen orthophosphate.

24. A multi-component product as claimed in claim 16 wherein the second aqueous solution comprises from 0.1% to 2% by weight of the second aqueous solution of said at least one hydrogen peroxide stabilizer.

25. A multi-component product as claimed in claim 28 wherein the second aqueous solution comprises from 0.2% to 1% by weight of the second aqueous solution of said at least one hydrogen peroxide stabilizer.

26. A multi-component product as claimed in claim 16 wherein said hydrogen peroxide stabilizer comprises cyclohexane-1, 2-diaminotetramethylenephosphonic acid or salt thereof.

27. A multi-component product as claimed in claim 16, 17, 18, 24 or 25, wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:5 to 1:50.

28. A multi-component product as claimed in claim 27 wherein the ratio of the volume of the first aqueous solution to the volume of the second aqueous solution is 1:10 to 1:30.

29. A multi-component product as claimed in claim 16, 17, 18, 24 or 25, wherein at least one of the first and second

aqueous solutions comprises an indicator which undergoes a colour change when the solutions are mixed together.

30. A multi-component product according to any one of claims 16, 17, 18, 24 or 25, wherein said phosphate corrosion inhibitor comprises a steel corrosion inhibitor.

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(11)

(12) UK Patent Application (19) GB (11) 2 182 051 (13) A

(43) Application published 7 May 1987

(21) Application No 8522416

(22) Date of filing 10 Sep 1985

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(51) INT CL<sup>4</sup>  
C11D 3/12 D06L 3/00

(52) Domestic classification (Edition I):  
CSD 6A5C 6A5D2 6A5E 6B12N1 6B12N2 6B12N3 6B12N5  
6B12NX 6B7 6B9 6C6 6D  
D1P 1113 1122 1307 1308 FB

(56) Documents cited  
GB A 2005715 GB 0696032 EP A1 0022023  
GB A 2000175 EP A1 0149264 US 4138051  
GB 1474856 EP A1 0028432 US 3769222

(58) Field of search  
CSD  
Selected US specifications from IPC sub-class C11D

(54) Stabilisation of peroxyacids in detergent compositions containing nonionic surfactant

(57) Peroxyacid stability in detergent compositions is assisted by adsorbing the nonionic surfactant onto smectite clays or pre-dried zeolites, to form particulate bodies which can then be mixed with the particulate peroxyacid. Suitable clays are sodium montmorillonite, and the hydrous magnesium silicates under the trademark "LAPONITE."

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## SPECIFICATION

## Stabilisation of peroxyacids

- 5 The present invention relates to the stabilisation of peroxyacids in compositions containing them, and more specifically to their stabilisation in the presence of nonionic surfactants. 5

Many particulate washing compositions or bleach additive compositions have contained a peroxygen compound as bleach. For many years, when it was common household washing practice to bring wash liquors to boiling point, the peroxygen compound has typically been a persalt such as sodium perborate (tetrahydrate or monohydrate) or sodium percarbonate. Those compounds are very effective bleaches at elevated washing temperatures but become less effective at the hand hot temperatures that are now being employed to a greater extent in view of changes in household fabrics, the finishes to them and the cost of heating water. In consequence, alternative peroxygen compounds have been sought that are more active at lower wash temperatures of which one important class comprises organic peroxyacids. Whilst it has been known that some peroxyacids are inherently more stable than others whilst in storage in particulate washing compositions, it has now been found also that a contributory factor in the destabilisation of even the most inherently stable peroxyacids is the presence of nonionic surfactants, common constituents of such compositions. 10 15

- 20 Accordingly, it is an object of the present invention to ameliorate the problem of nonionic surfactant-induced organic peroxyacid destabilisation. 20

According to the present invention there is provided a process for stabilising an organic peroxyacid in a nonionic surfactant-containing composition in which the nonionic surfactant is at least partly adsorbed by a particulate smectite clay or dried zeolite prior to its incorporation in the composition. 25

According to further aspects of the invention there are also provided bodies suitable for incorporation in particulate peroxyacid-containing compositions comprising a nonionic surfactant adsorbed on a particulate smectite clay or dried zeolite and compositions containing both a particulate peroxyacid and the aforementioned particulate bodies.

- 30 By the term smectite clay herein is meant clay minerals that are structurally derived intermediates between pyrophyllite  $\text{SigAl}_2\text{O}_{20}(\text{OH})_4$  and talc ( $\text{SigMg}_6\text{O}_{20}(\text{OH})_4$ ). In particular, the term encompasses montmorillonites and hectorites, with reference especially to alkali metal or alkaline earth metal montmorillonites or hectorites. It will be understood that herein naturally occurring clays which comprise mainly montmorillonite and/or hectorite, such as bentonite or fuller's earth can be readily employed in the instant invention process and compositions. Both swelling (i.e. high sodium) and non swelling (i.e. high calcium/magnesium) clays can be employed, and the latter may also have been acid treated to yield activated clay. It is especially suitable to employ substantially pure synthetic hydrous magnesium silicates (hectorites) available from Laporte Industries Limited under their own Trademark LAPONITE. Another eminently suitable clay a sodium montmorillonite is available under the trade mark VOLCLAY. The use of sodium or other alkali metal clays having a high calcium ion exchange capacity that enables the clay to act as a detergent builder in a washing solution is of particular value since it enables the surfactant carrier to perform a second useful role in any composition containing it. It has been found advantageous to pre-dry the clays before contacting them with the nonionic surfactants, especially employing a temperature at around or slightly above  $100^\circ$ , such as up to  $120^\circ\text{C}$ . The effect of such drying is to remove free water from the clays advantageously to below 2% w/w of the clay, and it may also encourage some activation. 35 40 45

- The second class of inorganic materials employed herein as adsorbant for the nonionic surfactant comprises zeolites, of which representative examples are zeolites A, X and Y and in particular the zeolites when in sodium form. Such zeolites are readily available in commerce. The various suitable crystalline zeolites and their characteristics are described in 'Zeolite Molecular Sieves' by Donald W. Beck published in 1974 by John Wiley and Sons. The reason why it is sensible to subject any zeolites to a prior drying stage as indicated for the clays, is that in the absence of a drying stage, adsorption of nonionic surfactant onto it can even accelerate the decomposition of any organic peracid mixed with the zeolite/surfactant bodies. It is advantageous to select any crystalline zeolites which are or have hitherto been recommended for use as detergent builders, that is to say have comparatively high calcium ion exchange capacity, since thereby the zeolite can provide a peracid stabilising role during storage and a builder role in use, enabling at least partial replacement of phosphate or other builders to occur. In that context, therefore, zeolites of formula  $\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \cdot 20\text{--}30 \text{ H}_2\text{O}$  before drying are also useful. 50 55 60

It is desirable to employ the adsorbent in fine powder form, and by way of example the powder is typically less than 1mm diameter, and preferably the greater part is below 0.8mm.

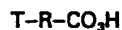
- The invention is applicable to any nonionic surfactant that is intended to be incorporated in a washing composition or bleach additive containing a peracid/detergent. The majority of such 65

surfactants are condensates of polyethylene oxide and/or other alkylene oxides such as propylene oxide with one or more hydrophobic moieties via an ether, ester, amino or amido linkage, i.e. by reaction with fatty alcohols, fatty acids, fatty amines and fatty amides. Fatty implies a carbon chain usually of at least 10 linear carbon atoms and often from 12 to 20. The number of ethylene oxide or other alkylene oxide units in the hydrophilic moiety is usually at least 3, often not in excess of 50, and in many instances is from 6 to 15 units on average. In a related class, the nonionic surfactant can comprise alkyl phenol or alkyl naphthol condensed with polyethylene oxide, in which the alkyl group usually comprises 8 to 12 linear carbon atoms, and at least 7, often 8 to 20 ethylene oxide units are employed. A further class of nonionic surfactants comprises fatty acid alkanolamides, and in particular mono or di ethanolamides and propanolamides.

The weight ratio of nonionic surfactant adsorbed by the smectite clay or zeolite is preferably less than that amount which leaves a sticky surface which would result in caking of the washing composition or bleach additive. The maximum amount for any combination of substrate and adsorbate varies depending especially on the nature and extent of pre-drying of the substrate, and can also depend on the physical size of adsorbate molecule. For many of the clays and zeolites the maximum preferred amount is to be found in the region of 30-45% by weight of the resultant bodies. Accordingly, various suitable bodies have the following compositions :-

- a) Montmorillonite 63-75% w/w  
nonionic surfactant 37-25% w/w
- b) dried montmorillonite 75-83% w/w  
nonionic surfactant 25-17% w/w
- c) 'LAPONITE' hectorite 57-70%  
nonionic surfactant 43-30%
- d) dried zeolite 80-85%  
nonionic surfactant 20-15%

Any solid organic peracid or salt can be employed in the instant invention, but it must be recognised that the improvement in storage stability obtained relates to any instability caused by interaction with the nonionic surfactant and not to the inherent stability or otherwise of the organic peracid. Most of the peroxyacids obey the general formula :-



in which R represents an alkylene group or an arylene group and T represents hydrogen or  $-CO_2M$ ,  $-CO_2M$  or  $-SO_3M$  in which M represents hydrogen or an alkali or alkaline earth metal. When R is aliphatic and T is hydrogen, R preferably contains 9 to 20 linear carbon atoms and when T is anything else R preferably contains 4 to 14 linear carbon atoms. Representative aliphatic peracids when T represents H include peroxydecanoic acid, and peroxydodecanoic acid, and when T represents  $-CO_2H$  or  $CO_2H$  respectively mono and di peroxy azelaic or dodecandioic acids, the diperoxy acids being abbreviated to DPA and DPDA. When R is arylene, the benzene nucleus can be unsubstituted, other than with the single  $-CO_2H$  group, or be substituted with a non-interfering group such as  $C_1$  to  $C_{20}$  alkyl, chloro or nitro groups, or a further carboxylic acid, peroxycarboxylic acid or sulphonic acid group or salt thereof. Examples of aromatic peracids include diperoxy isophthalic acid, monoperoxyphthalic acid and in particular the hydrated magnesium salt thereof (MMPP), 3-chloroperoxybenzoic acid and magnesium bis(3-chloroperoxybenzoate) and the monopotassium salt of 4-sulphoperoxybenzoic acid (KSPB).

It is especially desirable to employ peroxyacids or salts which have comparatively good inherent stability and these include MMPP, KSPB, DPA and DPDA.

The nonionic surfactant can be adsorbed on the clay or dried zeolite particles using a variety of techniques. In the simplest ways, the nonionic surfactant is agitated with the clay/zeolite particles at ambient temperature until it is apparent that the surfactant has been adsorbed. On a small scale this can be effected by gradually introducing more adsorbant into an agitated mixture, but on a large scale it is preferable to predetermine the relative amounts to use by using a small scale trial. Variations on the simple method can be employed, if desired, in which the surfactant, if solid at ambient temperature, is melted and the melt then mixed thoroughly with either preheated clay/zeolite whereby substantially complete adsorption can occur readily, or the entire mixture be heated to maintain that temperature, or alternatively the particles of clay/zeolite can be introduced cold whereby some of the surfactant can remain as a coating. Secondly, the surfactant can be introduced in a solvent preferably nonaqueous which is subsequently evaporated away. Whichever variation is used, though, the essential feature of the invention is that the surfactant is preadsorbed onto the clay/zeolite before being incorporated into the powder peroxyacid composition. Especially when at a larger scale, the surfactant after any necessary liquifaction by heating or dissolution can be sprayed into the clay or zeolite particles suitably agitated in a chamber by an inert fluidising gas such as air or by a vibrating pan surface or by a rotating inclined surface or drum. In a further technique, the surfactant and

adsorbant can be mixed as a slurry which is then spray dried by conventional apparatus.

The compositions can contain the peroxyacid and the surfactant/adsorbant bodies in any weight ratio at the discretion of the user. For many applications though, the weight ratio can be selected in the range of 5:1 to 1:20 peroxyacid: surfactant/adsorbant bodies, and to deliver into a washing solution efficacious amounts of both peroxyacid and surfactant, the ratio is often conveniently in the range 1:1 to 1:5.

Mixtures of the solid peroxyacid and surfactant bodies can be employed as such as bleaching compositions providing a lower than usual washing solution pH or alternatively they can be used as bleach additive compositions which are added to washing compositions at the point of use. Alternatively they can be incorporated directly in powder heavy duty detergent compositions. It will be recognised therefore that there is considerable overlap in function between the three aforementioned names for the compositions, and that the differences between them derive often from the omission of anionic surfactant and possibly detergent builders.

Bleaching or bleach additive compositions of the present invention often comprise from 0.5% to 50% w/w peroxyacid, from 99.5% to 40% w/w nonionic surfactant/adsorbant bodies and can also contain, if desired, a diluent up to 70% w/w of the composition. The diluent can be chosen from builders and processing aids detailed subsequently herein.

Washing compositions according to the present invention often contain 0.2 to 40% w/w peroxyacid, particularly 0.5 to 10% w/w, from 5 to 95% w/w surfactant of which at least part is provided in the form of nonionic surfactant adsorbed as herein described on a smectite clay or dried zeolite, and often from 5 to 40% w/w surfactant, from 0 to 90% builder, from 0 to 40% filler or processing aid, from 0 to 40% persalt, and from 0 to 20% in total of detergent auxiliaries.

The surfactants which can be employed in washing compositions according to the present invention or in conjunction with bleaching compositions according to the present invention can be nonionic and anionic, cationic or amphoteric. Generally, the surfactants contain at least one hydrophobic group, e.g. an aliphatic hydrocarbon group containing at least 8 carbon atoms, and often from 10 to 26 carbon atoms, the aliphatic group often being acyclic, but sometimes containing an alicyclic group, or the hydrophobic group can be an alkaryl group containing at least 6 and preferably up to 18 aliphatic carbon atoms. The surfactant contains in addition at least one water-solubilising group for example in anionic surfactants, it can be a sulphonate, sulphate, or carboxylic group which is linked either directly or indirectly to the hydrophobic group, and in nonionic surfactants it can be a poly(oxyethylene) chain. Linking members can include residues of polyhydric alcohols containing etheric or ester-linkages, for example derived from ethylene glycol, propylene glycol, glycerine or polyether residues. The surfactants can be soaps or be synthetic, for example as described in chapter 2 of Synthetic Detergents by A. Davidsohn and B.M. Mildwidsky, 5th Edition published in 1972 by Leonard Hill, London, and methods of making them are described in chapter 4 of the same book.

Amongst anionic surfactants described on pages 15-23 of the aforementioned book, sulphonates and sulphates are of special practical importance. The sulphonates include, for example, alkaryl sulphonates, and particularly alkyl benzene sulphonates, the alkyl group preferably being straight chain containing 9 to 15 carbon atoms, of which one of the most commonly employed surfactants is linear dodecyl benzene sulphonate. Other anionic sulphonates which are useful in washing compositions include olefin sulphonates, obtained, for example, by sulphonating primary or secondary aliphatic mono-olefins, alkene sulphonates, especially linear alkene sulphonates, and hydroxy alkene sulphonates and disulphonates, especially 3-, 4-, and 5-hydroxy-n-alkyl sulphonates in which the alkyl group contains any even number from 10 to 24 carbon atoms. Other desirable anionic surfactants include alcohol sulphates, preferably linear, having a chain length of at least 10 carbon atoms and sulphated fatty acid alkanolamides. Other sulphates comprise sulphated nonionic surfactants as for example alkylphenyl-ethylene oxide ether sulphate in which the alkyl groups contain from about 8 to 12 carbon atoms and there are 1 to 10 units of ethylene oxide in each molecule. Yet other sulphate surfactants comprise alkyl ether sulphates where the alkyl group contains from 10 to 20 carbon atoms, preferably linearly and each molecule contains from 1 to 10 preferably from 1 to 4 molecules of ethylene oxide. Further anionic surfactants include phosphate derivatives of the ethylene oxide based nonionic surfactants described herein.

In practice, cationic detergents are normally not present in the same composition as anionic surfactants, but when cationic detergents are used they are frequently quaternary ammonium salts such as tetraalkyl ammonium halides in which at least one of the alkyl group contains at least 10 carbon atoms or quaternary pyridinium salts substituted by an alkyl chain of at least 10 carbon atoms.

The nonionic surfactants usable herein have been described hereinbefore.

The nonionic and anionic surfactants are often employed together in many cases in a weight ratio within the range 2:1 to 1:10.

Useful amphoterics surfactants include derivatives of aliphatic quaternary ammonium, sulphonium

and phosphonium compounds in which the aliphatic moieties can be linear or branched, or two of which can join to form a cyclic compound, provided that at least one of the constituents comprises or contains a hydrophobic group containing from about 8 to 22 carbon atoms and the compound also contains an anionic water solubilising group, often selected from carboxylic, sulphate and sulphonates.

- 5 The builders, sometimes elsewhere alternatively called detergent builders or builder salts, which can be included in the washing compositions of the present invention can be either inorganic or organic and water-soluble or insoluble. Suitable inorganic builders are water-soluble include pyrophosphates, tripolyphosphates, and higher polymeric phosphates, having the formula
- 10  $\text{Na}_4\text{P}_2\text{O}_7(\text{MPO}_3)_n$ , where M represents an alkali metal cation and n is at least two. Other highly satisfactory inorganic builders include aluminosilicates which can act as cation exchangers for calcium and magnesium cations. Particularly suitable examples of aluminosilicates are zeolite A, characterised in USP 2 882 243, zeolite X characterised in USP 3013 990 and mixtures of A and X, preferably in a weight ratio of 50:50 to 15:35 and the zeolites disclosed in USP 3985
- 15 689. Other suitable inorganic builders include tetraborates, carbonates, bicarbonates and silicates. As is conventional, the inorganic builders are preferably in the form of the sodium salt. It will be recognised that the zeolites usable as builders also can act as adsorbants for the nonionic surfactants. Accordingly, in determining the weight of builder to employ, account can be taken of the weight of zeolite used as adsorbant.
- 20 The organic builders which are suitable for inclusion in washing compositions herein include hydroxycarboxylic acids, polycarboxylic acids, aminopoly carboxylic acids and polyphosphonic acids, it being recognised that, as with inorganic builders, the organic builders are normally employed in the form of the sodium salt thereof. It will be recognised that several of the builders could be ascribed to more than one of the classes of builders aforementioned. The
- 25 polycarboxylic acids can be monomeric such as  $\text{C}_2$  to  $\text{C}_{10}$  alpha-omega dicarboxylic acids, or  $\text{C}_3$  to  $\text{C}_9$  acyclic compounds substituted by at least three carboxylic acid groups such as 1,1,3,3-propane tetracarboxylic acid or 1,1,3,3,5,5-pentane-hexacarboxylic acid, or aromatic such as benzene pentacarboxylic acid. Alternatively, the polycarboxylic acid can be polymeric for example the polymers of acrylic acid, hydroxyacrylic acid, or maleic acid alone or copolymerised with one
- 30 another or with olefinically unsaturated compounds such as ethylene, vinyl alcohol, vinyl methyl ether, vinyl acetate or acrylamide. Other suitable polycarboxylates include so called "ether polycarboxylates" i.e. ethers in which both aliphatic moieties are short chain and each contains one or more carboxylic acid groups, such as oxydiacetic acid, oxydisuccinic acid or carboxymethyloxysuccinic acid. Alternatively the ether group forms part of a five membered oxole or oxolidine group which is substituted by carboxylic acid groups such as a furan tetracarboxylic acid or tetrahydrofuran tetracarboxylic acid.
- 35 By aminopolycarboxylic acid is meant amines that are substituted by a plurality of carboxylic acid groups, especially acetic acid groups and which may contain a plurality of amine nitrogen atoms linked by dimethylene groups. Such compounds include ethylene diaminetetraacetic acid, diethylene triaminepentaacetic acid, nitrilotriacetic acid and their counterparts in which one of the acetic acid groups is replaced by a (2-hydroxyethyl) group.
- 40 The polyphosphonic acids are normally alkyl, amino-, or hydroxyalkyl-polyphosphonic acid such as 1-aminoethane-1,1-diphosphonic acid, 1-amino-1-phenyl-1,1-diphosphonic acid, amino trimethylene-triphosphonic acid, ethylene diamino tetramethylenetetraphosphonic acid, 1-hydroxy ethane-1,1-diphosphonic acid. Related compounds containing one or more carboxylic acid groups can also be employed, such as 1-phosphonoethane-1,2-dicarboxylic acid.
- 45 The organic polycarboxylates, amino carboxylates and polyphosphonates and the corresponding acids are transition metal sequestrants and accordingly it can be beneficial to include a small amount of up to 5% w/w, e.g. 0.1 to 2% w/w together with the inorganic builders, especially
- 50 in the event that a persalt is present in the composition. The builder tends to produce a washing solution in the range of pH 7.5 to pH 10.5. Naturally, the washing composition can also contain auxiliary agents for washing compositions which are known in themselves such as soil anti-redeposition agents, dye transfer inhibitors, optical brightening agents, stabilisers for peroxyacids, corrosion inhibitors, bactericides, dyes,
- 55 perfumes, foam enhancers, foam inhibitors, absorbents and abrasives. Such auxiliary agents are often present to a total amount of up to 20% by weight of the washing composition, and typically at least 1% and frequently between 1 and 10%.
- By way of example, sodium carboxymethylcellulose is of practical importance as a soil antiredeposition agent, and derivatives of diaminostilbene sulphonic acid and 1,3-diaryl-2-pyrazolines, and aminocoumarins are well known optical brighteners.
- 60 If desired, the washing composition can contain in addition one or more inorganic persalts such as sodium perborate monohydrate, or sodium percarbonate, for example in a mole ratio to peracid of preferably over 1:1 to 5:1. Such a combination can be particularly desirable where the washing composition is dissolved in the washing liquor at ambient temperature and the liquor is
- 65 then heated to a final washing temperature in excess of 60 to 70°C, the peracid providing an

oxidising bleach at low washing temperatures and the persalt remaining to continue the bleaching at the high washing temperatures. If desired, auxiliaries in the washing compositions of the present invention can include an aldehyde or ketone peroxyacid activator as described in USP 4005 029, e.g. 8-hydroxy quinoline which is also a well known peroxygen stabiliser.

- 5 Washing processes according to the present invention can be carried out at a temperature from ambient up to the boiling point of the washing solution. Compositions according to the present invention are particularly well suited to a process at which washing or bleaching is carried out by steeping at ambient or by heating the solution to a temperature from about 25° to 60°C. Alternatively the washing and bleaching processes may be effected by heating up a cold washing solution. A combination of processes can be used, such as cold steeping followed by a wash at 30, 40 or 50°C. 10

In general, it is desirable for washing or bleaching solutions for use in the home to contain at least 1 part per million available oxygen (Avox) preferably at least 5 parts per million Avox.

- Household washing solutions prepared by dissolution of detergent compositions in general provide no more than about 200 ppm Avox, frequently no more than 100 ppm Avox and in many cases in the range of 25 to 200 ppm Avox. 15

In general, the rate of removal of stains is enhanced by employing a higher temperature and by higher Avox concentrations. The contact period between solution and fabric can conveniently be as short as 5 minutes. Longer periods of for example, up to 1 hour tend to provide greater soil removal. In cold washing or steeping even longer periods can be employed, such as steeping overnight. 20

- In addition to washing and/or bleaching fabrics, the compositions can be used to clean hard surfaces such as metal, plastic or wooden surfaces, either by dissolving washing or bleaching compositions in water, preferably to provide 200 ppm to 500ppm avox or by forming a slurry or paste of such compositions. Also, if desired, solutions produced by the dissolution of compositions described herein can be used to bleach textile fabrics, wood or pulp bleaching such articles with hydrogen peroxide or inorganic peroxyacids. 25

Having described the invention in general terms, specific embodiments will be described more fully by way of example.

- 30

#### Examples

Examples 1 to 5 and Comparisons 6 and 7

- In these Examples and Comparisons bodies of nonionic surfactant and adsorbant were prepared by stirring into a representative nonionic surfactant (alcohol ethoxylate, ether residue C12-C14, degree of ethoxylation 7) a powdered adsorbant, introduced slowly, until all the surfactant had been taken up by the adsorbant, judged by eye. The resultant products were free-flowing particulate bodies having the compositions summarised by Table 1 below. VOLCLAY and LAPONITE are Trade Marks of respectively Allied Colloids and Laporte Industries Limited. 35

	Adsorbant Type	% wt in bodies	
		Adsorbant	Surfactant
40 Ex 1	Montmorillonite (detergent grade)	63	37
45 Ex 2	Montmorillonite (detergent grade) predried	76	24
Ex 3	"VOLCLAY"	64	36
Ex 4	Predried zeolite Y	80	20
Ex 5	"LAPONITE" RD	57	43
50 C6	Zeolite Y	67	33
C7	Sodium carbonate	71	29

From Table 1 it can be seen that the adsorbants were able to take up a substantial weight of surfactant.

- 55 Examples 8 to 12 and Comparisons 13 to 15 55

In these Examples and Comparisons 13, 14 the bodies produced in the preceding Examples and Comparisons were mixed with a particulate peroxyacid salt, magnesium monoperoxyphthalate hexa-hydrate available from Interlox Chemicals Limited under their trademark Interlox H48. In Comparison 15, the surfactant was present as such, i.e. not preadsorbed onto any substrate.

- 60 Each mixture contained the nonionic surfactant in a weight ratio to the H48 peroxy acid salt of 1.5:1. The mixtures were then stored at 37°C in "Polybottles" (Trade Mark for polyethylene bottles, 100 ml size) with pinholes in the cap to permit gases to vent off, and the peracid available oxygen was measured periodically by arsenious oxide oxidation followed by back titration with iodine technique. The results after two weeks storage are shown in Table 2 below, 65 computed as % Avox lost, except for C14 which was after 1 week's storage only. 65

Table 2

	Product of	% Avox lost	
Ex 8	Ex 1	38	
5 Ex 9	Ex 2	8	5
Ex 10	Ex 3	3	
Ex 11	Ex 4	31	
Ex 12	Ex 5	0	
C13	C6	99	
10 C14	C7	73*	10
C15	not adsorbed	76	

From Table 2, it can be seen that when the nonionic surfactant is preadsorbed onto certain adsorbents, the rate at which available oxygen is lost from the peracid can be reduced, in some instances by a very substantial extent. Thus, by comparing Ex 8 with Ex 9, and Ex 11 with C13, it will be seen that predrying the adsorbent substantially improved the peracid stability when the adsorbent was either the montmorillonite clay or the zeolite. Indeed, in the case of the zeolite the body produced by adsorbing nonionic surfactant onto the non-predried material appeared to accelerate peracid decompositions as can be seen by comparing C13 with C15. Moreover, by comparing C14 with C15 it will be seen also that some substrates which could adsorb a similar amount of nonionic surfactant also accelerated peracid decomposition. On the other hand, very good stability improvement was achieved by adsorbing onto predried montmorillonite and excellent improvement using VOLCLAY and LAPONITE adsorbents.

#### 25 Comparisons 16 and 17

By way of further comparisons, trials were made in which 0.85 parts by weight of the same peracid salt and 0 or 1 part by weight of the adsorbent of Example 5 were simply mixed in particulate form into 5 parts by weight of a detergent composition containing the same nonionic surfactant (20% w/w) and in addition 5% w/w anionic surfactant, 60% w/w sodium tripolyphosphate, 10% w/w sodium silicate, 5% w/w sodium sulphate and 2% detergent auxiliaries including an OBA and SARD. The mixtures were stored at 37°C in pinholed "Polybottles" as in Examples/Comparisons 8 to 15, and the residual avox measured periodically as before. After 4 weeks storage of the "LAPONITE"-free composition, (C16) the peracid had lost 42% of its Avox, whereas in the "LAPONITE"-containing composition (C17) the peracid had lost 43% of its Avox. Both results are so similar that post adding of the adsorbent to the mixture gives no detectable benefit. This result is completely different from when the surfactant was pre-adsorbed into the LAPONITE adsorbent when the Avox loss was reduced from 76% to virtually zero.

#### CLAIMS

- 40 1. A nonionic surfactant-containing composition in which the nonionic surfactant is at least partly adsorbed by a particulate smectite clay or dried zeolite prior to its incorporation in the composition.
2. A process according to claim 1 in which the adsorbent is a montmorillonite or hectorite clay.
- 45 3. A process according to claim 2 in which bodies are formed by the adsorption of 37-25% w/w nonionic surfactant onto 63-75% w/w montmorillonite or 43-30% w/w nonionic surfactant onto 57-70% w/w hectorite.
4. A process according to claim 1 or 2 in which the adsorbent is a pre-dried clay.
5. A process according to claim 4 in which bodies are formed by the adsorption of 25-17% w/w nonionic surfactant onto 75 to 83% w/w pre-dried clay.
- 50 6. A process according to claim 1 in which the zeolite is A, X or Y.
7. A process according to claim 1 or 6 in which bodies are formed by absorbing 20-15% w/w nonionic surfactant onto 80-85% w/w pre-dried zeolite.
8. A process according to any preceding claim in which the clay or zeolite has a high calcium-ion exchange capacity.
- 55 9. A process according to any preceding claim in which a liquid or molten nonionic surfactant is contacted with the particulate adsorbent and agitated until a free-flowing mass is obtained, or the nonionic surfactant is introduced in non-aqueous solution onto the adsorbent and the solvent evaporated off with agitation of the mixture.
- 60 10. A process according to any preceding claim in which the nonionic surfactant is a condensate of polyethylene oxide with a hydrophobic alkyl, aralkyl or alkaryl moiety via an ether, ester, amino or amido linkage.
11. A process according to claim 10 in which the surfactant is a condensate of alkyl phenol or alkyl naphthol or C10-C20 fatty alcohol with polyethylene oxide.
- 65 12. Bodies of nonionic surfactant adsorbed on a particulate smectite or predried zeolite as

described in any preceding claim.

13. A bleaching or bleach additive composition comprising a mixture of bodies according to claim 12 with an organic peroxyacid.

14. A composition according to claim 13 in which the peroxyacid is diperoxyazelaic acid, diperoxydodecanedioic acid, magnesium monoperoxyphthalate hexahydrate, or potassium-4-sulphoperoxybenzoic acid. 5

15. A composition according to claim 13 or 14 and further containing one or more anionic surfactants, and optionally one or more detergent builders, processing aids or detergent auxiliaries.

10 16. A composition according to claim 15 which comprises 0.2 to 40% peroxyacid, 5 to 95% surfactant of which the nonionic part is adsorbed in a smectite clay or predried zeolite, 0 to 90% builder, 0 to 40% processing aid, 0 to 40% persalt and 0 to 20% detergent auxiliaries. 10

17. Means for stabilising an organic peroxyacid in nonionic surfactant-containing compositions substantially as described herein with respect to any novel feature or novel combination of 15 features, and compositions containing an organic peroxyacid so stabilised. 15

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon) Ltd, Dd 8991685, 1987.  
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.